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Molecular Weight Comparisons from Density and X-Ray Data. The Atomic Weights of Calcium and Fluorine

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Molecular weights have been compared by combination of the x-ray and density data for the crystals, calcite, diamond, lithium fluoride, sodium chloride, and potassium chloride. By assumption of the chemical atomic weights of carbon, chlorine, potassium, lithium, and sodium, values for the atomic weights of calcium and fluorine have been calculated. The method employed consists of a series of independent calculations from the results of which final weighted average values have been taken for the atomic weights of calcium and fluorine. This has yielded 40.0849 ± 0.0030 and 18.9967 ± 0.0013, respectively. These values are most probably the most precise values for these constants at the present time. From the results of the present work it becomes apparent that the determination of atomic weights from comparison of molecular weights by combination of density and x-ray data is as reliable as other standard atomic weight procedures.

I. INTRODUCTION

MOLECULAR weights have been compared previously[1-4] by combination of density and x-ray data. For the comparison of the molecular weights of two crystalline substances, there must be known the values of the absolute densities, the ratio of the true x-ray grating spaces, and the arrangement of molecules in the unit cell of each substance. The comparison can be expressed by means of the relationship,

$$M_1 = M_2\{(\rho_1/\rho_2)FR_g^3\}. \quad (1)$$

The numerical subscripts refer to the two crystalline substances, the molecular weights of which are compared; M is a molecular or atomic weight; ρ is a density; F is a factor determined by the crystal structures; and R_g is the ratio of the true x-ray grating spaces of the two crystals.

C. A. Hutchison and H. L. Johnston[1] have used Eq. (1) to compare the molecular weights of lithium fluoride and calcite. With the assumption of the atomic weights of calcium, carbon, and lithium, they were able to obtain an atomic weight for fluorine. H. L. Johnston and the writer[2] have obtained an atomic weight for fluorine utilizing the data on lithium fluoride and sodium chloride and assuming the atomic weights of lithium, sodium, and chlorine. C. A. Hutchison[3] has calculated the atomic weight of calcium utilizing the data on calcite and diamond and assuming the atomic weight of carbon. From this value for calcium and that assumed for carbon, he has calculated the atomic weight of fluorine. Recently, the writer[4] reported values for the

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[1] C. A. Hutchison and H. L. Johnston, J. Am. Chem. Soc 63, 1580 (1941).
[2] H. L. Johnston and D. A. Hutchison, Phys. Rev. 62, 32 (1942).
[3] C. A. Hutchison, J. Chem. Phys. 10, 489 (1942).
[4] D. A. Hutchison, Phys. Rev. 66, 144 (1944).

TABLE I. Density and x-ray data corrected to 20°C for certain selected crystals used in the comparison of molecular weights.

Data designation	Substance	$\rho_{20°C}$(g/cm³)	$\vartheta_{20°C}$(degrees)	$\delta\times10^6$	n	Reflecting plane	$\alpha\times10^5$(linear)
A	LiF	2.64030[a] ±0.00014	83°51′15.7″±0.5[f]	7.91	3	111	3.41[i]
B	Calcite	2.71030[b] ±0.00005	6°42′34.9″±0.3[g,h] 27°51′32.1±0.3[b]	1.85	1 4	Natural Cleavage	1.04[k]
C	Diamond	3.51540[c] 0.00006	23°26′5.8″±0.5[g]	2.39	1	100	0.118[l]
D	NaCl	2.16360[d] ±0.00004	15°51′4.4″±0.8[i]	1.41	1	100	4.05[m]
E	KCl	1.98827[e] ±0.00004	6°28′25.8″±0.4[g]	1.32	1	100	3.77[n]

[a] C. A. Hutchison and H. L. Johnston, J. Am. Chem. Soc. **62**, 3165 (1940).
[b] J. A. Bearden, Phys. Rev. **38**, 2089 (1931). Bearden gives this density value as the best mean of his value and that of Defoe and Compton, Phys. Rev. **25**, 618 (1925).
[c] J. A. Bearden, Phys. Rev. **54**, 698 (1938).
[d] H. L. Johnston and D. A. Hutchison, Phys. Rev. **62**, 32 (1942).
[e] D. A. Hutchison, Phys. Rev. **66**, 144 (1944).
[f] Straumanis, Ievins and Karlsons, Zeits. f. physik. Chemie **B42**, 143 (1939).
[g] Y. Tu, Phys. Rev. **40**, 622 (1932).
[h] Larsson, Phil. Mag. [7] **3**, 1136 (1927).
[i] M. Siegbahn, Ann. d. physik **BD59**, 56 (1919).
[j] Adenstadt, Ann. d. physik **26**, 69 (1936).
[k] Larsson, Inaugural-Dissertation, Uppsala (1929).
[l] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1927), Vol. 3, p. 21.
[m] Straumanis and Ievins, Zeits. f. Physik **102**, 353 (1936); Straumanis, Ievins, and Karlsons, Zeits. f. anorg. allgem. Chemie **238**, 175 (1938).
[n] Klemm, Tilk, and Mullenheim, Zeits. f. anorg. allgem. Chemie **176**, 1 (1928).

atomic weights of calcium and fluorine which were calculated from the x-ray and density data for calcite, lithium fluoride, and potassium chloride.

The R_g's used in the present work were calculated directly from the primary data, the x-ray reflection angles, as were those of C. A. Hutchison.[3] Since the values of the R_g's, F's, and ρ's have been determined with high precision for the five crystalline substances used in the present calculations, it is possible to compare the molecular weights of these substances with high precision.

If sufficient x-ray data were available, it would be possible to compose a system of x-ray-density atomic weights which would be independent of chemical determinations of atomic weights. Since a set of crystals cannot be found which would give an atomic weight system based on oxygen, and independent of atomic weights from other sources, we may refer to the results of the present calculations as x-ray-density-chemical atomic weights.

The purpose of the present paper is the presentation of the method of calculating and the results obtained for the atomic weights of calcium and fluorine utilizing the x-ray and density data for the five crystalline substances, calcite, diamond, lithium fluoride, sodium chloride, and potassium chloride.

TABLE II. Chemical atomic weights employed in the calculations.

Symbol	Value
C	12.0104±0.0002[a]
Cl	35.4570±0.0005[b]
K	39.0960±0.0005[c]
Li	6.9390±0.0002[d]
Na	(1)22.9970±0.0005[b]

[a] This value is a mean of all the good combustion analyses of Baxter and Hale and is in good agreement with that of Scott and Hurley.
(1) Baxter and Hale, J. Am. Chem. Soc. **59**, 506 (1937).
(2) Scott and Hurley, J. Am. Chem. Soc. **59**, 1905 (1937).
[b] (1) Richards and Wells, "A Revision of the Atomic Weights of Sodium and Chlorine," Carnegie Institution of Washington, Publication No. 28 (1905).
(2) Noyes and Weber, J. Am. Chem. Soc. **30**, 13 (1908).
(3) Zintl and Meuwsen, Zeits. f. anorg. allgem. Chemie **136**, 223 (1924).
(4) Honigschmid, Chan, and Birckenbach, Zeits. f. anorg. allgem. Chemie **163**, 315 (1927).
(5) Honigschmid and Sachtleben, Zeits. f. anorg. allgem. Chemie **178**, 1 (1929).
(6) Scott and Johnson, J. Phys. Chem. **33**, 1975 (1929).
(7) Honigschmid, J. Am. Chem. Soc. **53**, 3012 (1931).
[c] (1) Richards and Stahler, J. Am. Chem. Soc. **29**, 623 (1907).
(2) Richards and Mueller, J. Am. Chem. Soc. **29**, 639 (1907).
(3) Baxter and MacNevin, J. Am. Chem. Soc. **55**, 3185 (1933).
(4) Honigschmid and Sachtleben, Zeits. f. anorg. allgem. Chemie **213**, 365 (1933).
(5) McAlpine and Bird, J. Am. Chem. Soc. **63**, 2960 (1941).
[d] (1) Richards and Willard, J. Am. Chem. Soc. **32**, 4 (1910); Zeits. f. anorg. allgem. Chemie **66**, 229 (1910).
(2) Carnegie Institution Publication No. 25, 1 (1910).

TABLE III. The atomic weight of calcium.

Calculation No.	Data for mol. wt. comparison from Table I	F	R_ϑ	R_λ	Calc'd. at. wt.	Chem. at. wt. on which calc'd. value is dependent
1	$\frac{M_{\text{calcite}}(B)}{M_{\text{NaCl}}(D)}$	1.09594 ±0.00001	1.076443 ±0.000020	0.4604078 ±0.0000021	40.0851 ±0.0059	Na, Cl, C
2	$\frac{M_{\text{calcite}}(B)}{M_{\text{KCl}}(E)}$	1.09594 ±0.00001	0.965029 ±0.000020	1.000000 ±0.000014	40.0851 ±0.0067	K, Cl, C
3	$\frac{M_{\text{calcite}}(B)}{M_{\text{diamond}}(C)}$	0.273985 ±0.000003	3.404303 ±0.000046	1.000000 ±0.000014	40.0844 ±0.0052	C
4	$\frac{M_{\text{calcite}}(B)}{M_{\text{LiF}}(A)}$	1.09594 ±0.00001	1.508187 ±0.000021	0.4604078 ±0.0000021	40.0850 ±0.0064	K, Cl, Li C, Na

Most probable value (weighted average) of atomic weight of calcium—40.0849 ±0.0030.

TABLE IV. The atomic weight of fluorine.

Calculation No.	Data for mol. wt. comparison from Table I	F	R_ϑ	R_λ	Calc'd. at. wt.	Chem. at. wt. on which calc'd. value is dependent
5	$\frac{M_{\text{LiF}}(A)}{M_{\text{KCl}}(E)}$	1.000000 ±0.000000	0.639860 ±0.000023	2.1719872 ±0.0000098	18.9967 ±0.0031	K, Cl, Li
6	$\frac{M_{\text{LiF}}(A)}{M_{\text{NaCl}}(D)}$	1.000000 ±0.000000	0.713733 ±0.000012	1.000000 ±0.000018	18.9967 ±0.0021	Na, Cl, Li
7	$\frac{M_{\text{LiF}}(A)}{M_{\text{diamond}}(C)}$	2.000000 ±0.000000	1.128610 ±0.000047	2.1719872 ±0.0000098	18.9967 ±0.0027	Li, C
8	$\frac{M_{\text{LiF}}(A)}{M_{\text{calcite}}(B)}$	0.9124587 ±0.0000083	0.663048 ±0.000015	2.1719872 ±0.0000098	18.9967 ±0.0028	Na, Cl, C Li, K

Most probable value (weighted average) of atomic weight of fluorine—18.9967 ±0.0013.

II. DATA FOR THE MOLECULAR WEIGHT COMPARISONS AND ATOMIC WEIGHT CALCULATIONS

The quantities necessary for the molecular weight comparisons have been corrected to 20°C and the values listed in Table I. The density of each substance at 20°C has been computed from the most probable reported values by means of the cubical coefficient of expansion, which is three times the linear expansion coefficient listed in column eight of Table I. The reflection angle, ϑ, for each crystal at 20°C has been obtained from the most probable literature value by means of the expression,

$$\log \sin \vartheta_{20^\circ} = \log \sin \vartheta_t - (\alpha(20-t)/2.303), \quad (2)$$

where t is the temperature at which the reflection angle is reported in the literature and α is the linear coefficient of expansion given in column eight of Table I. δ, the unit decrement of the index of refraction of a crystal, is defined by the expression, $\delta = 1 - \mu$, where μ is the index of refraction. The values of the δ's given in column five of Table I were calculated by means of the expression,

$$\delta = (ne^2\lambda^2)/(2\pi mc^2), \quad (3)$$

which assumes the wave-lengths used to be much shorter than any critical absorption wave-length of the crystals involved. n is the total number of electrons per cubic centimeter, and other symbols have their usual meaning. Column six of Table I gives the order of the reflection angles and column seven, the reflecting plane.

In the calculations of the atomic weights, certain chemical atomic weights have been assumed. The values for these chemical atomic weights are listed in Table II.

In all instances of these original data, reported values were surveyed critically, and, where necessary, recalculations from original data were made and arbitrary weights, based on the internal and external consistency of the reported data, were assigned to obtain most probable values.

III. CALCULATIONS OF THE ATOMIC WEIGHTS

In considering the best method of attacking the problem of getting the most probable values for the atomic weights of calcium and fluorine from the available x-ray and density data, two methods are at one's disposal.

One method involves a series of stepwise computations from which each atomic weight obtained is dependent on the preceding computation. If there are given the densities, ρ's, and the x-ray reflection angles, ϑ's, for the five crystalline substances given in Table I, any four of the corresponding molecular weights may be computed from the remaining one. From certain sets of three assumed chemical atomic weights (no less than three atomic weights can be chosen), the remaining four atomic weights can be computed. This method cannot be used since, in any given series of stepwise calculations to obtain best values for the atomic weights of calcium or fluorine, the final probable error is so great that the purpose of the calculations is defeated.

Another method consists of a series of independent calculations, from which a final weighted average value can be obtained. The latter is the method chosen for the calculations presented here. The results of each independent calculation are presented in Tables III and IV.

Let us take as an example of these calculations the computation of the atomic weight of fluorine, listed as computation number 5 in Table IV, which utilizes the x-ray and density data for lithium fluoride (A) and potassium chloride (E). Equation (1) becomes in this case,

$$M_{\mathrm{F}}=\frac{\rho_{\mathrm{LiF}}R_0^{3}FM_{\mathrm{KCl}}}{\rho_{\mathrm{KCl}}}-M_{\mathrm{Li}}. \qquad (4)$$

The R_0 has been computed by means of the expression,

$$R_0=\frac{n_1R_\lambda \sin\vartheta_2(1-\delta_2/\sin^2\vartheta_2)\xi}{n_2\sin\vartheta_1(1-\delta_1/\sin^2\vartheta_1)}, \qquad (5)$$

where the subscripts "1" refer to data on lithium fluoride and the subscripts "2" refer to data on potassium chloride. ξ is a factor which corrects for the fact that x-ray reflection angles are not from corresponding planes in the two crystals; R_λ[5] is the ratio of the wave-lengths employed in the determination of x-ray reflection angles; the other symbols have their usual meaning as given in the introduction.

Other data employed in Eq. (4) are listed in Table I. Since both crystals have the sodium chloride type structure, the value of F becomes unity. It is seen in columns six and seven of Table IV that the calculated atomic weight for fluorine, 18.9967 ± 0.0031, is dependent on the chemical atomic weights of chlorine, potassium, and lithium.

The results of the series of independent calculations for calcium are given in Table III, and those for fluorine in Table IV. Their probable errors have been obtained in the usual manner by application of the law for propagation of errors,

$$p_U^{2}=\left(\frac{\partial U}{\partial x}\right)^{2}p_x^{2}+\left(\frac{\partial U}{\partial y}\right)^{2}p^{2}y+\cdots, \qquad (6)$$

where $U=f(x, y, \cdots)$.

In order to utilize the x-ray and density data for lithium fluoride in the determination of the atomic weight of calcium (see calculation number 4 of Table III), a weighted average was taken for the atomic weight of fluorine from the results obtained in the first three computations of Table IV. This result, 18.9967 ± 0.0015, is not dependent on an atomic weight of calcium. This procedure makes possible the use of all available data and reduces the error of the final adopted value for the atomic weight of calcium by ten parts per million.

In a similar manner the data on calcite have been used to obtain an atomic weight for fluorine (see calculation number 8 of Table IV). The weighted average, 40.0848 ± 0.0034, obtained from the results of the first three calculations of Table III, has been used in calculation number 8. Thus, in this case all data have been employed and the final adopted value for the probable error

[5] R_λ was calculated from the reflection angles for the Cu$K\alpha_1$ line and Mo$K\alpha_1$ line from calcite as obtained by J. A. Bearden and C. H. Shaw, Phys. Rev. **48**, 18 (1935) and Larsson, Phil. Mag. [7] **3**, 1136 (1927).

in the atomic weight of fluorine is reduced by nine parts per million.

The writer has observed from results obtained in carrying out these computations that x-ray angles from "powder" method data are definitely less trustworthy than angles obtained by the Bragg reflection method even though great improvements have been made on the "powder" method by Straumanis and co-workers.[6] For this reason "powder" data have been excluded from this work except where they were the only data available.

A possible source of error[6] in these computations lay in the uncertainty in the thermal coefficients of expansion of the crystals involved. With reduction of density and x-ray data to 20°C, it was necessary to make correction for the uncertainties of the thermal coefficients. Each coefficient was considered separately; but in all, the correction amounted to multiplying the probable error assigned by the original investigator by a factor of approximately 2.

With this description of the calculation procedures, one may consult the summary of results of individual calculations in column six of Tables III and IV.

The final most probable value for each atomic weight is a weighted average based on the probable errors of the results of the individual calculations. The final adopted value for calcium is 40.0849 ± 0.0030 and for fluorine is 18.9967 ± 0.0013. The probable errors are based on the internal consistency of the results of the individual calculations. For calcium the error amounts to 75 parts per million and for fluorine to 68 parts per million. These appear to be definite improvements over previously published values. The probable error obtained from the external consistency of individual results can be seen to be very small compared to that obtained from the internal consistency. The adopted probable error is the larger of the two. Since theory predicts that the ratio of these two values should not differ from unity by more than about 28 percent, it can be concluded that too great allowance has been made for systematic errors in the original data and that the adopted probable error is somewhat greater than the true probable error.

[6] This observation has been made previously by R. T. Birge in connection with his work on the value of the Avogadro number. R. T. Birge, Am. J. Phys. **13**, 63–67 (1945).

IV. CONCLUSIONS

If the density and x-ray data are utilized to obtain other atomic weights, one obtains excellent checks between the chemical atomic weights and the calculated values. In view of these close checks between chemical and calculated atomic weights as well as the method employed in these calculations, considerable weight can be attached to the results for the atomic weights of calcium and fluorine obtained here.

It will be seen that the value obtained for calcium, 40.0849 ± 0.0030, is in close agreement with the value 40.085, obtained by Honigschmid and Kempter.[7] It is somewhat higher than the recent value, 40.080 ± 0.005, given by Birge[8] and is in disagreement with the older value of Richards and Honigschmid[9] and the more recent value of Kendall, Smith, and Tait.[10]

The atomic weight, 18.9967 ± 0.0013, obtained for fluorine is in close agreement with the gas-density value, 18.997, of Cawood and Patterson[11] using fluoroform, but in disagreement with their value, 18.995, using carbon tetrafluoride. It is in disagreement with the gas density value of Moles and Toral,[12] using silicon tetrafluoride and in disagreement with the mass spectrographic value, 18.999.[13]

It is apparent that the determination of atomic weights from the comparison of molecular weights by combination of density and x-ray data is as reliable as other standard atomic weight procedures.

[7] Honigschmid and Kempter, Zeits. f. anorg. allgem. Chemie **195**, 1 (1931).
[8] R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941).
[9] Richards and Honigschmid, J. Am. Chem. Soc. **32**, 1577 (1910).
[10] Kendall, Smith, and Tait, Nature **131**, 688 (1933).
[11] Cawood and Patterson, Trans. Roy. Soc. (London) **A236**, 77 (1936).
[12] Moles and Toral, Zeits. f. anorg. allgem. Chemie **236**, 225 (1938).
[13] A. K. Brewer, Phys. Rev. **49**, 867 (1936).

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Force Constants of Triatomic Molecules

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In the general expression of the potential energy of the triatomic molecule XYZ there are six force constants c_1, c_1' (valence bond), c_2 (angle deformation), c_3, c_3' (angle bond interaction), and c_4 (bond-bond interaction), of which only three can be calculated from the three experimentally determined fundamental frequencies. For the isosceles triatomic molecule YX_2 the number of force constants reduces to four (c_1, c_2, c_3, and c_4). From a study of *all* the *real* values of these four force constants, it is seen that they are related to one another by ellipses and straight lines. The graphs of these ellipses indicate the possibility of choosing a certain singular point (near one end of the major axis) which gives the following relation between the force constants:

$$dc_4/dc_2=0 \quad \text{or} \quad dc_4/dc_3=0.$$

This condition *and* the equations usually obtained from the theory of small vibrations permit the calculation of a singular set of four force constants of the isosceles triatomic molecule. When these force constants are applied to isotopic molecules, satisfactory checks between the calculated and experimentally determined frequencies are obtained.

The ellipses showing the relation between the force constants indicate clearly why the *simple central force field* (c_1, c_2, c_3) or the *simple valence force field* (c_1, c_2, c_3), containing one interaction constant or crossterm, must yield imaginary values for c_2 and c_3 in certain cases.

INTRODUCTION

THE theory of small vibrations[1,2] leads to equations connecting the fundamental frequencies of a molecule and the force constants, masses, distances, and angles of its structure. These equations can be used to calculate the force constants if other quantities are known. It happens quite frequently that fewer frequencies are available than the number of force constants which it is desirable to know. The triatomic molecule has only three fundamental frequencies, and, hence, only three force constants can be determined. Two cases are usually dealt with: the central force field and the valency force field. Since the latter views of atomic interaction agree with the ideas of chemical valence, they are used most frequently and also in the following considerations. For the general triatomic molecule XYZ the six constants are: valence bond (c_1, c_1'); angle bending (c_2); angle-bond interaction (c_3, c_3'); and bond-bond interaction (c_4). For the isosceles triatomic molecule the four force constants are c_1, c_2, c_3, and c_4. If the constant c_4 is neglected ($c_4=0$), the case can be called the *simple* valency force field (c_1, c_2, c_3) and these three constants can be determined from the three fundamental frequencies. However it happens quite often that no consistent set (c_1, c_2, c_3) can be found, and c_2 and c_3 turn out to be imaginary. Any new method which would furnish additional information permitting the evaluation of the *four* force constants of the isosceles triatomic molecule, even though only *three* frequencies are available would be of some value and should be investigated. Such an empirical method is considered in this study. The process is as follows: All of the real values of the four force constants are calculated by allowing c_4 to have all possible values which do not lead to imaginary numbers for c_2 and c_3. These real values are shown in Figs. 1–6 and 8, as ellipses and straight lines. It is seen that an infinite number of sets (c_1, c_2, c_3, c_4) can be found that satisfy the initial equations of the theory of small vibrations. However, it is felt that one of these sets might be distinctive, and the essence of this study is to find this special case. It is expected that the bond force constant c_1 in a given molecule should be of the same order of magnitude as the force constant of the corresponding diatomic molecule. For example the bond constant of OH in the water molecule may be expected to be similar in magnitude to the one for the same atoms in hydroxyl radical.

In the case of water and deuterium oxide, it

* A thesis submitted in partial fulfillment of the requirements for the degree of master of science, in the Department of Chemistry and Chemical Engineering, in the Graduate College of the State University of Iowa.

[1] K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Verlagsbuchhandlung, Julius Springer, Berlin, 1931).

[2] G. Glockler, "The Raman Effect," Rev. Mod. Phys. **15**, 111 (1943).

was found that the ellipses obtained from the respective frequencies are nearly alike (Fig. 1, full and dotted lines).[2] Since c_4 is an interaction constant it may be surmised that its value should be small in magnitude. From an inspection of these ellipses it appears that points near one of the ends of the major axes might offer a satisfactory choice of one distinctive set of all four force constants from the infinite number of sets. One such singular point is given by the condition

$$dc_4/dc_2=0 \quad \text{or} \quad dc_4/dc_3=0. \tag{1}$$

It turns out that this choice also yields a value for c_1 which seems reasonable. The other similar point near the other end of the major axes refers to a much larger absolute value of c_4 and a value for c_1 which is very different from the force constant c_1 of the related diatomic molecule. Hence this set is disregarded. The program of this study is then to *calculate all real sets of four force constants for triatomic isosceles molecules from the three equations of the theory of small vibrations using the three known frequencies and then applying condition (1) to choose one distinctive set.* The force constants so determined are then used to calculate the three frequencies of *isotopic* molecules which can be compared with experiment.

THEORY OF SMALL VIBRATIONS

Only a few salient features will be mentioned since this topic has been discussed often.[1,2] The potential energy expression (V) of the general triatomic molecule (XYZ) can be written in terms of cartesian displacements:

$$\begin{aligned}2V=&c_1\cdot\Delta_{21}^2+c_1'\cdot\Delta_{31}^2+c_2\cdot r_{21}\cdot r_{31}\cdot\Delta\alpha^2\\&+2c_3\cdot r_{21}\cdot\Delta\alpha\cdot\Delta_{21}+2c_3'\cdot r_{31}\cdot\Delta\alpha\cdot\Delta_{31}\\&+2c_4\cdot\Delta_{21}\cdot\Delta_{31}.\end{aligned}\tag{2}$$

The force constants have been defined above and

Δ_{21}, Δ_{31} = small bond displacements,
$\Delta\alpha$ = small angle deformation,
r_{21}, r_{31} = equilibrium bond lengths.

From Eq. (2) and from the kinetic energy (T) of the system

$$2T=\textstyle\sum_i m_i(\dot{x}_i^2+\dot{y}_i^2),$$

it is possible to write the Lagrangian equation of motion

$$d(\partial L/\partial\dot{q}_i)/dt+\partial L/\partial q_i=0,$$

where $L=T-V$, q_i is any coordinate and the m_i refers to the masses of the atoms. From these relations determinantal equations are derived from which force constants can be calculated.

The determinant of the general triatomic molecule is given for comparison with the special cases of the isosceles structure, the linear symmetrical molecule and the linear asymmetrical case. Some examples of each type have been examined.

GENERAL TRIATOMIC MOLECULE

The determinantal equation can be written

$$\begin{vmatrix}\lambda-L_{11} & -L_{21} & -L_{31}\\ -L_{12} & \lambda-L_{22} & -L_{32}\\ -L_{13} & -L_{23} & \lambda-L_{33}\end{vmatrix}=0, \tag{3}$$

where

$$-L_{11}=-c_1/\mu_{21}+(c_3/m_1)(r_{21}/r_{31})^{\frac{1}{2}}\sin\alpha-(c_4/m_1)\cos\alpha,$$

$$-L_{12}=-(c_1/m_1)\cos\alpha+(c_3/m_1)(r_{31}/r_{21})^{\frac{1}{2}}\sin\alpha-c_4/\mu_{31},$$

$$-L_{13}=(c_1/m_1)(r_{21}/r_{31})^{\frac{1}{2}}\sin\alpha-c_3[(1/m_1)(r_{32}^2/r_{21}r_{31})+(1/m_2)(r_{31}/r_{21})+(1/m_3)\cdot(r_{21}/r_{31})]+(c_4/m_1)(r_{31}/r_{21})^{\frac{1}{2}}\sin\alpha,$$

$$-L_{21}=-(c_1'/m_1)\cos\alpha+(c_3'/m_1)(r_{21}/r_{31})^{\frac{1}{2}}\sin\alpha-c_4/\mu_{21},$$

$$-L_{22}=-c_1'/\mu_{31}+(c_3'/m_1)(r_{31}/r_{21})^{\frac{1}{2}}\sin\alpha-(c_4/m_1)\cos\alpha,$$

$$-L_{23}=(c_1'/m_1)(r_{31}/r_{21})^{\frac{1}{2}}\sin\alpha-c_3'[(1/m_1)(r_{32}^2/r_{21}r_{31})+(1/m_2)(r_{31}/r_{21})+(1/m_3)\cdot(r_{21}/r_{31})]+(c_4/m_1)(r_{21}/r_{31})^{\frac{1}{2}}\sin\alpha,$$

$$-L_{31}=(c_2/m_1)(r_{21}/r_{31})^{\frac{1}{2}}\sin\alpha-c_3/\mu_{21}-(c_3'/m_1)\cos\alpha,$$

$$-L_{32}=(c_2/m_1)(r_{31}/r_{21})^{\frac{1}{2}}\sin\alpha-(c_3/m_1)\cos\alpha-c_3'/\mu_{31},$$

$$-L_{33}=-c_2[(1/m_1)(r_{32}^2/r_{21}r_{31})+(1/m_2)(r_{31}/r_{21})+(1/m_3)(r_{21}/r_{31})]$$
$$+(c_3/m_1)(r_{21}/r_{31})^{\frac{1}{2}}\sin\alpha+(c_3'/m_1)(r_{31}/r_{21})^{\frac{1}{2}}\sin\alpha;$$

where $1/\mu_{21}=1/m_2+1/m_1$, $1/\mu_{31}=1/m_3+1/m_1$; m_1 is the mass of the central atom. Expanding this determinant and comparing it with the general cubic equation yields

$$\lambda_1+\lambda_2+\lambda_3=L_{11}+L_{22}+L_{33},$$
$$\lambda_1\lambda_2+\lambda_1\lambda_3+\lambda_2\lambda_3=L_{11}L_{22}+L_{11}L_{33}+L_{22}L_{33}-L_{13}L_{31}-L_{23}L_{32}-L_{12}L_{21}, \quad (4)$$
$$\lambda_1\lambda_2\lambda_3=L_{11}L_{22}L_{33}-L_{22}L_{13}L_{31}-L_{11}L_{23}L_{32}-L_{33}L_{12}L_{21}+L_{13}L_{21}L_{32}+L_{12}L_{23}L_{31}.$$

Only three force constants contained in the L_{ij}'s can be determined assuming that the valence angle α and the bond distances r_{21} and r_{31} can be obtained from other sources such as data on electron diffraction. The weights of the atoms are labeled as follows: Y(m_1 or M); X(m_2 or m); and Z(m_3 or m).

ISOSCELES TRIATOMIC MOLECULE

In this case, $c_1=c_1'$, $c_3=c_3'$, $r_{21}=r_{31}$, $m_1=M$, $m_2=m_3=m$, and $1/\mu=1/M+1/m$. The quantities L_{ij} reduce to

$$-L_{11}=-L_{22}=-c_1/\mu$$
$$+(c_3/M)\sin\alpha-(c_4/M)\cos\alpha,$$

$$-L_{12}=-L_{21}=-(c_1/M)\cos\alpha$$
$$+(c_3/M)\sin\alpha-c_4/\mu,$$

$$-L_{13}=-L_{23}=(c_1/M)\sin\alpha$$
$$-2c_3[1/\mu-\cos\alpha/M]+(c_4/M)\sin\alpha,$$

$$-L_{31}=-L_{32}=(c_2/M)\sin\alpha-c_3[1/\mu+\cos\alpha/M],$$

$$-L_{33}=-2c_2[1/\mu-\cos\alpha/M]+2(c_3/M)\sin\alpha.$$

From the determinantal equation, it is seen that

$$\lambda_1+\lambda_2=L_{11}+L_{12}+L_{33},$$
$$\lambda_1\lambda_2=L_{33}(L_{11}+L_{12})-2L_{13}L_{31}, \quad (5)$$
$$\lambda_3=L_{11}-L_{12}.$$

With the use of Eqs. (5) *and* the special condition (Eq. (1)), the four force constants of water molecule have been determined from its three fundamental frequencies. Since the force constants of deuterium oxide are the same as for the water molecule, they can now be used to

TABLE I. Calculated frequencies of deuterium oxide vapor molecule.

	Experiment (cm^{-1})[a]	Calculation (cm^{-1})
ω_3	2883.79	2883.51
ω_1	2758.06	2758.76
ω_2	1210.25	1209.99

[a] D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

TABLE II. Real values of the force constants of the water vapor molecule (megadynes/cm), (i=imaginary).

c_1	c_2		c_4	c_3	
0.8485	i	i	0	i	i
0.8386	0.0763	0.0763	−0.0099	0.0234	0.0234
0.8385	0.0768	0.0759	−0.0100	0.0277	0.0192
0.7985	0.1270	0.1028	−0.0500	0.1284	−0.0861
0.7485	0.1797	0.1465	−0.1000	0.1650	−0.1283
0.6485	0.2781	0.2410	−0.2000	0.1770	−0.1516
0.5485	0.3689	0.3430	−0.3000	0.1216	−0.1076
0.5017	0.4011	0.4011	−0.3468	0.0044	0.0044
0.4985	i	i	−0.3500	i	i

TABLE III. Experimental frequencies of isosceles triatomic molecules.

Molecule	Angle α	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})
H_2O	104°31′	3825.32	1653.91	3935.39[a]
H_2S	92°20′	2615	1265	2630[b]
$>CH_2$	115°	2970	1444	3000[c]
SO_2	120°	1152	524	1361[b]

[a] D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).
[b] See reference 6.
[c] W. G. Penney and G. B. B. M. Sutherland, Proc. Roy. Soc. **A156**, 654 (1936).

TABLE IV. Calculated force constants of isosceles triatomic molecules. (megadynes/cm).

Molecules	c_1	c_2	c_3	c_4
H_2O	0.8386	0.0763	0.0234	−0.0099
H_2S	0.3942	0.0460	0.0060	−0.0016
$>CH_2$	0.4874	0.0562	0.0170	0.0123
SO_2	1.0416	0.1069	0.1346	0.0479

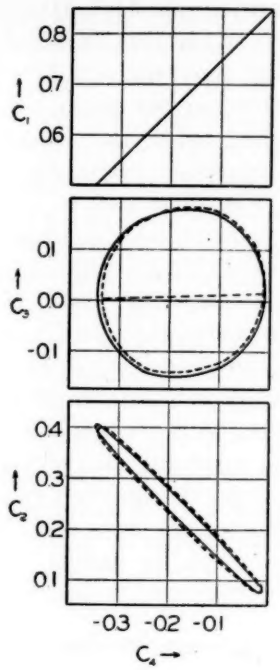

FIG. 1. Relation between force constants of water and deuterium oxide (megadynes/cm). (Dotted D_2O, and full line H_2O).

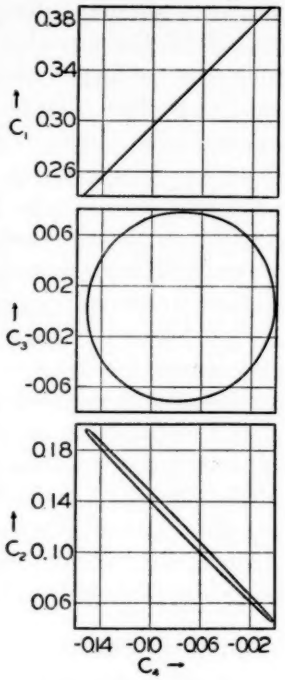

FIG. 2. Relation between force constants of hydrogen sulfide molecule (megadynes/cm).

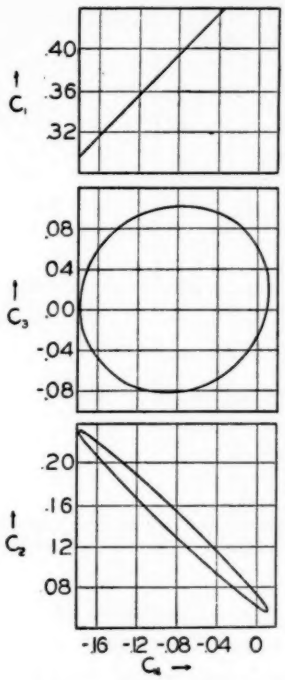

FIG. 3. Relation between force constants of the methylene radical (megadynes/cm).

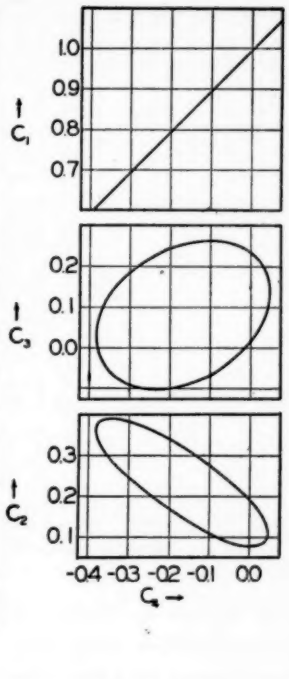

FIG. 4. Relation between force constants of the sulfur dioxide molecule (megadynes/cm).

calculate the fundamental frequencies of deuterium oxide as shown in Table I. It is seen that the calculated values check the experimental frequencies most satisfactorily. It appears that the smallest absolute value of c_4 (-0.0099) represents a satisfactory singular point, being near one end of the two major axes of both ellipses. This special point is represented by condition (Eq. (1)). The other extreme of the two major axes ($c_4=-0.3468$) would yield a value for c_1 very markedly different from the force constant for the diatomic hydroxyl radical (OH). From the above relations the following explicit expressions of the force constants can be derived:

$$\begin{aligned} c_1&=\lambda_3/2C+(C\lambda_1)/[2(AC-B^2)],\\ c_2&=\lambda_2/2C+(B^2\lambda_1)/[2C(AC-B^2)],\\ c_3&=(B\lambda_1)/[2(AC-B^2)],\\ c_4&=c_1-\lambda_3/C, \end{aligned} \tag{6}$$

where $A=1/\mu+\cos\alpha/M$; $B=\sin\alpha/M$; $C=1/\mu-\cos\alpha/M$. A sample calculation is shown in Table II. It can readily be seen that the simple valency force field without the interaction force constant (i.e., $c_4=0$) leads to imaginary values of the force constants c_2 and c_3.

In this manner several molecules of this type have been studied. The experimental frequencies used are collected in Table III. From them the force constants of these molecules were calculated (Table IV) and their respective ellipses indicating the relations between their force constants, are shown in Figs. 1–4. The force constants mentioned in Table IV have been used to calculate the frequencies of certain isotope molecules

TABLE V. Comparison of experimental and calculated frequencies of isosceles triatomic molecules.

Molecules	ω_1 Exp. (cm^{-1})	ω_1 Cal. (cm^{-1})	ω_2 Exp. (cm^{-1})	ω_2 Cal. (cm^{-1})	ω_3 Exp. (cm^{-1})	ω_3 Cal. (cm^{-1})
HDO	2720	2818.60	1403	1407.41	—	3882.68[a,b,c]
D_2O	2758.06	2758.76	1210.25	1209.99	2883.79	2883.51[d]
HDS	—	1881.87	1090	1090.99	—	2622.06[e]
D_2S	1891.6	1864.02	934	930.92	2000	1889.49[e,f]
$>CD_2$	—	2140.66	—	1072.00	—	2232.27
>CHD	—	2186.34	—	1214.00	—	2984.82
$>C^{13}H_2$	—	2965.27	—	1438.08	—	2988.20

[a] See reference 3.
[b] See reference 4.
[c] See reference 5.
[d] D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).
[e] A. H. Nielsen and H. H. Nielsen, J. Chem. Phys. 5, 277 (1937).
[f] G. M. Murphy and J. E. Vance, J. Chem. Phys. 6, 426 (1938).

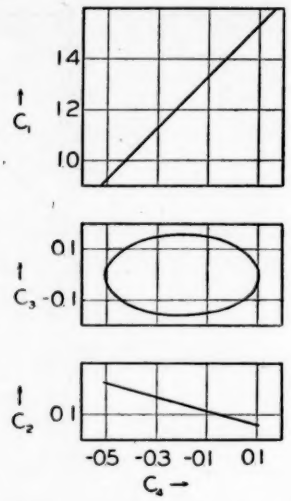

FIG. 5. Relation between force constants of the carbon dioxide molecule (megadynes/cm).

as shown in Table V. The calculation of the deformation frequency ω_2 of the hybrid water molecule (HDO) checks experiment satisfactorily. On the other hand a discrepancy exists between calculation and experiment in the case of the symmetric frequency ω_1. The experimental value of ω_1 is given by Barker and Sleator[3] as 2720 cm^{-1}. On the other hand calculations by Libby[4] and by Shaffer and Schuman[5] yield 2818.1 cm^{-1} and 2820.3 cm^{-1} for this frequency. These values are not based on the method discussed here. The present calculations yield 2818.6 cm^{-1}. Hence these three calculations agree among themselves but they do not check the experimental value. It must mean that the infra-red band at 2720 cm^{-1} needs to be reinterpreted. The frequency ω_2 of the hybrid hydrogen sulphide molecule (HDS) checks with experiment very well. For deutero-hydrogen sulphide (D_2S) ω_1 and ω_2 check reasonably well although the difference between experimental and calculated values for ω_3 needs further attention.

The calculated frequencies of the methylene radical ($>CH_2$) and its isotopic relatives ($>CHD$, $>CD_2$) show among themselves the same relations as the corresponding isotopic water molecules (H_2O, HDO, and D_2O) and the similar hydrogen sulfide structures (H_2S, HDS, and D_2S). The introduction of the first deuteron into the ordinary proton molecule (H_2X, $X=C, O, S$) has a large effect on the frequency ω_1 ($\Delta\omega_1=784$, 1006, 733 cm^{-1}) while the sec[illegible] deuteron changes the frequency very li[illegible] ($\Delta\omega_1=46$, 60, 17 cm^{-1}). The deformation [illegible]quency ω_2 varies regularly by a few hundreds wave numbers (first deuteron: $\Delta\omega_2=230$, 2[illegible], 174 cm^{-1}; second deuteron: $\Delta\omega_2=142$, 197, 159 cm^{-1}). The asymmetric frequency ω_3 shows just the opposite effect to ω_1. Introducing the first deuteron into the ordinary proton structure has only a small effect ($\Delta\omega_3=16$, 53, 8 cm^{-1}) while a second deuteron changes ω_3 markedly ($\Delta\omega_3=753$, 1000, 733 cm^{-1}). Substituting C^{13} into the CH_2-radical does not affect either of the three fundamental frequencies very much as might be expected (Table V).

LINEAR SYMMETRICAL TRIATOMIC MOLECULE

In this case, $c_1=c_1'$, $c_3=c_3'$, the valency angle $\alpha=180°$ and $r_{32}=r_{31}+r_{21}=2r_{31}=2r_{21}$. The quantities L_{ij} reduce to

$$-L_{11}=-L_{22}=-c_1/\mu+c_4/M,$$
$$-L_{12}=-L_{21}=c_1/M-c_4/\mu,$$
$$-L_{13}=-L_{23}=-2c_3[1/\mu+1/M],$$
$$-L_{31}=-L_{32}=-c_3/m,$$
$$-L_{33}=-2c_2[1/\mu+1/M].$$

The carbon dioxide and carbon disulphide molecules whose experimental frequencies are

TABLE VI. Experimental frequencies of linear symmetrical triatomic molecules.

Molecules	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})
CO_2	1321.7	667.9	2362.8[a]
CS_2	655.0	397.0	1522.0[b]

[a] T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Prentice-Hall, Inc., New York, 1941).
[b] See reference 6.

TABLE VII. Calculated force constants of linear symmetrical triatomic molecules (megadynes/cm).

Molecules	c_1	c_2	c_3	c_4
CO_2	1.5339	0.0571	0	0.1052
CS_2	0.7467	0.0234	0	0.0598

[3] E. F. Barker and W. W. Sleator, J. Chem. Phys. **3**, 660 (1935).
[4] W. F. Libby, J. Chem. Phys. **11**, 101 (1943).
[5] W. H. Shaffer and R. P. Schuman, J. Chem. Phys. **12**, 504 (1944).

shown in Table VI have the force constants mentioned in Table VII. By their use the isotopic molecules $C^{13}O_2$ and $C^{13}S_2$ were calculated as shown in Table VIII. Only the asymmetric frequency ω_3 of $C^{13}O_2$ can be compared with experiment. The check seems satisfactory. The relation between the force constants are shown in Figs. 5 and 6. It is seen that the angle-bond interaction constant (c_3) is related to the bond-bond interaction constant (c_4) by an ellipse whose major axis is parallel to the c_4-axis and that c_3 is equal to zero. This feature is true in both instances and may therefore be taken to be the case for linear molecules. The angle deformation force constant c_2 is related linearly to the constant c_4. In this case the usual ellipse reduced to a straight line.

TABLE VIII. Calculated frequencies of linear symmetrical triatomic molecules.

Molecules	ω_1 Exp. (cm^{-1})	ω_1 Cal. (cm^{-1})	ω_2 Exp. (cm^{-1})	ω_2 Cal. (cm^{-1})	ω_3 Exp. (cm^{-1})	ω_3 Cal. (cm^{-1})
$C^{13}O_2$	—	1321.70	—	649.01	2284.5	2295.97[a]
$C^{13}S_2$	—	655	—	383.96	—	1472.02

[a] A. H. Nielsen, Phys. Rev. **53**, 983 (1938).

LINEAR ASYMMETRIC TRIATOMIC MOLECULES

Of the six force constants, c_3 and c_3' are taken to be zero on the assumption that this feature can be extended from carbon dioxide and carbon disulfide, even though the molecule ($m_2m_1m_3$) is not symmetrical as for example OCS, although linear. The quantities L_{ij} become:

$$-L_{11}=-c_1/\mu_{21}+c_4/m_1,$$
$$-L_{12}=+c_1/m_1-c_4/\mu_{31},$$
$$-L_{13}=0,$$
$$-L_{21}=+c_1'/m_1-c_4/\mu_{21},$$
$$-L_{22}=-c_1'/\mu_{31}+c_4/m_1,$$
$$-L_{23}=0,$$
$$-L_{31}=0,$$
$$-L_{32}=0,$$
$$-L_{33}=-c_2[(1/m_1)(r_{32}^2/(r_{31}r_{21}))+(1/m_2)(r_{31}/r_{21})+(1/m_3)(r_{21}/r_{31})].$$

The determinant can now be written as follows:

$$\begin{vmatrix} \lambda-L_{11} & -L_{21} & 0 \\ -L_{12} & \lambda-L_{22} & 0 \\ 0 & 0 & \lambda-L_{33} \end{vmatrix}=0.$$

Expanding and comparing with the general quadratic equation yields

$$\lambda_2=L_{33},$$
$$\lambda_1+\lambda_3=L_{11}+L_{22}, \quad (7)$$
$$\lambda_1\lambda_3=L_{11}L_{22}-L_{12}L_{21}.$$

An attempt was made to find another relation as described above between the force constants c_1, c_1', and c_4 which would make it possible to calculate the three force constants from the two frequencies ω_1 and ω_3. By analogy the following conditions were assumed

$$dc_4/dc_1=0 \quad \text{and} \quad dc_4/dc_1'=0. \quad (8)$$

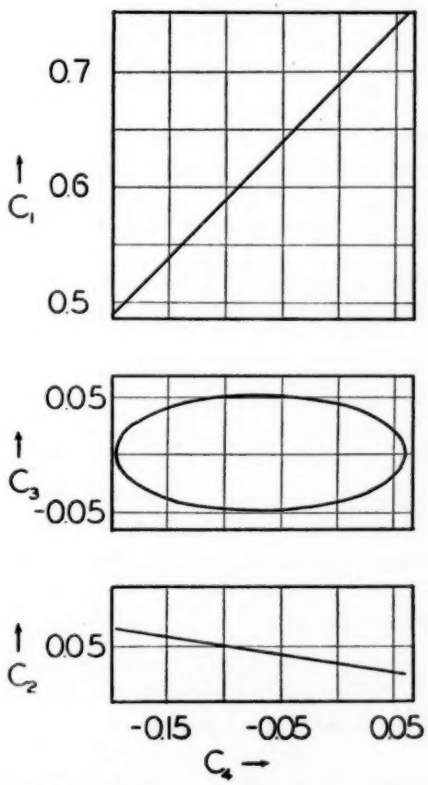

FIG. 6. Relation between force constants of the carbon disulfide molecule (megadynes/cm).

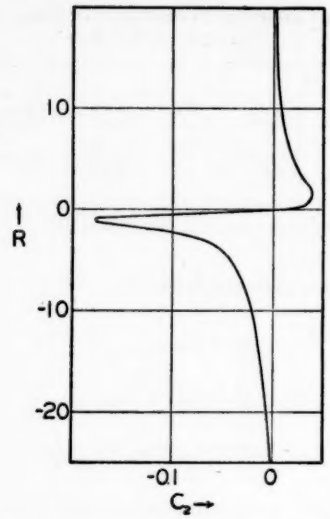

FIG. 7. Relation between ratio (R) of atomic distance of C=O, and C=S. ($R=r_{C=O}/r_{C=S}$) and the angle force constant "c_2" (megadynes/cm).

The last two statements in Eq. (7) can be written

$$(\lambda_1+\lambda_3)\mu_{31}c_1-(\mu_{31}/\mu_{21})c_1^2 +(2\mu_{31}/m_1)c_1c_4-c_4^2 =\lambda_1\lambda_3/[(1/\mu_{31}\mu_{21})-(1/m_1^2)]. \quad (9)$$

Differentiating Eq. (9) gives dc_4/dc_1 and using the condition Eq. (8) yields

$$(\lambda_1+\lambda_3)\mu_{31}-2(\mu_{31}/\mu_{21})c_1+2(\mu_{31}/m_1)c_4=0. \quad (10)$$

Substitution of Eq. (10) into Eq. (9) gives the following explicit values of the four force constants:

$$\begin{aligned}
c_1&=[\{-m_1(\lambda_1+\lambda_3)+(\mu_{21}\mu_{31})^{\frac{1}{2}} \times(\lambda_1-\lambda_3)\}\mu_{21}m_1]\div[2(\mu_{21}\mu_{31}-m_1^2)],\\
c_1'&=[\{-m_1(\lambda_1+\lambda_3)+(\mu_{21}\mu_{31})^{\frac{1}{2}} \times(\lambda_1-\lambda_3)\}\mu_{31}m_1]\div[2(\mu_{21}\mu_{31}-m_1^2)],\\
c_2&=\lambda_2[(1/\mu_{31})(r_{21}/r_{31}) +(1/\mu_{21})(r_{31}/r_{21})+2/m_1]^{-1},\\
c_4&=[\{-\mu_{21}\mu_{31}(\lambda_1+\lambda_3)+(\mu_{21}\mu_{31})^{\frac{1}{2}} \times(\lambda_1-\lambda_3)m_1\}m_1]\div[2(\mu_{21}\mu_{31}-m_1^2)].
\end{aligned} \quad (11)$$

The carbonyl sulphide molecule (COS) was investigated by using the following frequencies:

$$\omega_1(859),\quad \omega_2(527),\quad \omega_3(2079\ \text{cm}^{-1});^{6}$$
$$r_{C=O}(1.151),\quad r_{C=S}(1.538\text{A});^{7-10}$$

The ratio $R(=r_{C=O}/r_{C=S}=0.7484)$ yields the force constant $c_2=0.0364$ (megadyne/cm). This value is not as close to the average (0.0402) of the c_2-values of carbon dioxide (0.0571) and of carbon disulphide (0.0234) (megadyne/cm) as one might expect for the COS molecule. However an investigation of the relationship between R and c_2 (Eq. (11)) shows that the average value of c_2 (0.0402) is not compatible with any real

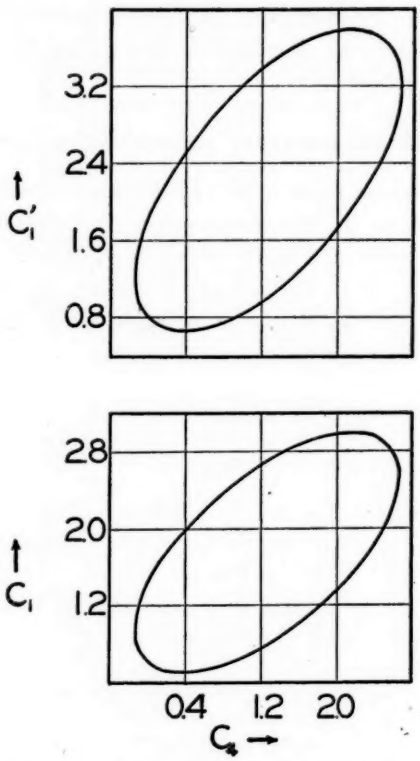

FIG. 8. Relation between force constants of the carbonyl sulfide molecule. c_1=CO-bond force constant and c_1'=CS bond force constant (megadynes/cm).

[6] H. Sponer, *Molekülspektren und ihre Anwendung auf chemische Probleme* (Verlagsbuchhandlung, Julius Springer, Berlin, 1936).
[7] W. Jevons, *Band Spectra of Diatomic Molecules* (University Press, Cambridge, 1932).
[8] H. A. Stuart, *Molekül Struktur* (Verlagsbuchhandlung, Julius Springer, Berlin, 1934).
[9] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).
[10] G. Herzberg, *Molecular Spectra and Molecular Structure* I. *Diatomic Molecules* (Prentice-Hall Inc., New York, 1934). II. *Infrared and Raman Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

value of the ratio R. The relation is shown in Fig. 7. The ratio R for the largest and smallest value of c_2 were found by differentiation to be

$$R=\pm(\mu_{31}\mu_{21})^{\frac{1}{2}}. \qquad (12)$$

Substituting numerical values:

$R[c_2\ (\text{max.})]=1.1285$;

$c_2=0.0383$ megadyne/cm.

$R[c_2\ (\text{min.})]=-1.1285$;

$c_2=-0.1774$ megadyne/cm.

Neither of these values of R is satisfactory for they would lead to impossible values of either the C=O or C=S distance in carbonyl sulphide. Hence c_2 calculated from Eq. (11) has been accepted as 0.0364 megadyne/cm. The other force constants for the COS molecule are shown in Fig. 8 and from Eq. (11) were found to be: $c_1=0.9461$, $c_1'=1.2049$, and $c_4=-0.1252$.

The two bond force constants (c_1 and c_1') show however an unexpectedly large change from the corresponding constants of CO_2 ($c_1=1.5335$) and CS_2 (0.7456). Hence, the conditions Eq. (8) are not satisfactory for this triatomic molecule. In the present case another procedure was adopted. It may be expected that the interaction constant c_4 for COS should not differ greatly from the mean of the corresponding constants for CO_2 ($c_4=0.10522$) and for CS_2 ($c_4=0.05934$). This mean value for COS would be 0.08228, yielding for COS the constant $c_1=1.5593$ and $c_1'=0.7243$. Another method of estimating the interaction constant (c_4) for COS is to assume that the bond constant c_1 for CO_2 (1.5335) remains the same in COS, yielding an interaction c_4 for COS equal to 0.06707, and similarly that the force constant c_1' for CS_2 (0.7456) also remains the same in COS. This proposal yields $c_4=0.05333$ for COS. The average of these values of c_4 for COS (0.06707 and 0.05333) or 0.06019 permits the calculation of c_1 for COS (1.52159) and c_1' (0.74015). Either of these sets fits into Badger's rule[11] as can be seen from Fig. 9 and Table IX. In the case of the CO-bond a reasonably good straight line is obtained considering the fact that the interatomic distances are not known accurately in most cases. For the CS-bond only three cases are known, insufficient to draw a satisfactory straight line. But a line drawn parallel to the CO-line fits the CS-points well enough. The force constants c_1 (0.9461) and c_1' (1.2049) would not fit into this scheme at all. Hence the most reasonable values for the force constants of COS are c_1 (1.5216), c_1' (0.7401), c_2 (0.0364), c_3 (0), c_3' (0), and c_4 (0.6019) megadynes/cm.

TABLE IX. Force constants and interatomic distance. Badger's rule.[a]

Molecule	ω (cm^{-1})	c_1 (megadynes per cm)	$c_1^{-1/3}$	r (A°)	Remarks
CO($A\ ^1\Pi$)	1517	0.9248	1.0264	1.232	[b]
CO(>C=C—C=O)	1660	1.1080	0.9664	1.21	[c,d]
CO(>C=O)	1700	1.1560	0.9528	1.21	[c,d]
CO(COS)	2079	0.9461	1.0186	1.16	$c_4=-0.1252$ [f,g,h]
CO(COS)	2079	1.5593	0.8624	1.16	$c_4=0.0823$
CO(COS)	2079	1.5216	0.8694	1.16	$c_4=0.06019$
CO(CO_2)	2363	1.5335	0.8671	1.15	[f,g,d]
CO($^1\Sigma^+$)	2168	1.8886	0.8090	1.128	[j]
CO($B\ ^1\Sigma$)	2182	1.9141	0.8054	1.118	[b]
CS(COS)	2079	1.2049	0.9616	1.56	$c_4=-0.1252$ [f,g,h]
CS(COS)	2079	0.7248	1.1130	1.56	$c_4=0.0823$
CS(COS)	2079	0.7401	1.1055	1.56	$c_4=0.06019$
CS(CS_2)	1522	0.7456	1.1028	1.54	[f,g,d,h]
CS($^1\Sigma^+$)	1285	0.8416	1.0592	1.536	[j]

[a] See reference 11.
[b] See reference 7.
[c] J. H. Hibben, *The Raman Effect and Its Application* (Reinhold Publishing Corporation, New York, 1939).
[d] See reference 9.
[e] See reference 1.
[f] See reference 6.
[g] See reference 8.
[h] L. O. Brockway, Rev. Mod. Phys. 8, 231 (1936).
[i] T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Prentice-Hall, Inc., New York, 1941).
[j] See reference 10.

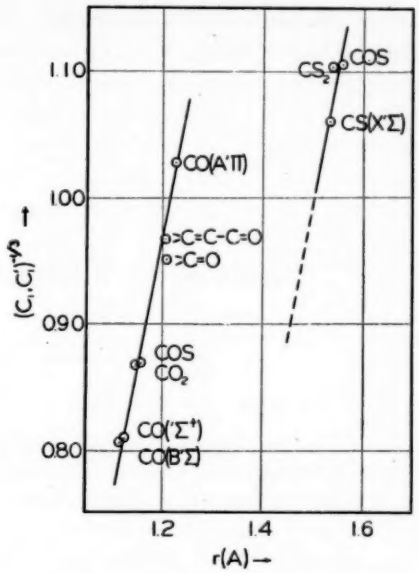

FIG. 9. Badger's rule for CO and CS.

[11] R. M. Badger, J. Chem. Phys. 2, 128 (1934); 3, 710 (1935).

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Theory of the Ultraviolet Absorption Spectrum of Diphenyl*

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The lower excited energy levels of the molecule diphenyl are calculated by the method of antisymmetrized products of molecular orbitals. The wave functions for diphenyl are constructed from linear combinations of benzene molecular orbitals and the perturbation of the original energy levels of benzene caused by the presence of the second benzene ring in diphenyl is computed. The theory predicts the splitting of the two non-degenerate singlet levels and the one degenerate singlet level of benzene into eight levels, four of which give allowed electronic transitions to the ground state and four of which do not. Experimentally three strong structureless bands are observed, one between $\lambda=2200$A and $\lambda=2800$A, one at about $\lambda=1900$A, and one below $\lambda=1700$A. The calculated spectrum has allowed transitions at about 2400A, 1900A, 1500A, and 1400A, and thus is in good agreement with the experimental observations.

I. INTRODUCTION

IN a previous paper[1] the method of antisymmetrical molecular orbitals has been applied to a calculation of the lower excited electronic energy levels of benzene. The results obtained from this calculation have been extensively compared to experiment; analysis of the observed spectrum[2] indicates good agreement between the theory and experiment. Since benzene is one of the simplest of aromatic compounds, it was decided to extend the usefulness of the results obtained in the benzene case to other more complicated molecules having benzene as a structural element. Sklar[3] has considered the case of the ultraviolet absorption of singly and of multiply substituted benzenes. Here, we consider the case of diphenyl which is a special case of a substituted benzene in which one hydrogen atom is replaced by another benzene ring (minus one hydrogen atom).

For the purposes of this calculation, it is assumed that the molecule is flat, i.e., the benzene rings are coplanar. A number of investigators have discussed this point. Dhar has concluded from x-ray studies[4] of diphenyl that the molecule is flat and that any deviation from planarity, if it exists, is less than 0.1A. Dipole moment[5] investigations of para-dinitro and para-dichloro derivatives of diphenyl by Smythe and others have indicated that diphenyl is flat. H. de Laszlo[6] has obtained electron diffaction patterns of diiododiphenyl which are in agreement with the planar diphenyl structure.

Pauling[7] has discussed the possibility that the two benzene rings in diphenyl are twisted with respect to each other about the longitudinal axis located in the mean plane of the molecule.

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[1] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938). Abbreviation GMS used in future references to this paper.

[2] H. Sponer, G. Nordheim, A. L. Sklar, E. Teller, J. Chem. Phys. **7**, 207 (1939); F. K. Herzfeld, Proc. Am. Phil. Soc. **82**, 359 (1940).

[3] A. L. Sklar, J. Chem. Phys. **7**, 984 (1939).

[4] J. Dhar, Indian J. Phys. **7**, 43 (1932); J. Hengstenberg and H. Mark, Zeits. f. Krist. **70**, 283 (1929).

[5] C. P. Smythe, Ind. Eng. Chem. **23**, 224 (1931); A. Weissberger, R. Sängewald, and G. C. Hampson, Trans. Faraday Soc. **30**, 884 (1934).

[6] H. deLaszlo, Trans. Faraday Soc. **30**, 884 and 892 (1934).

[7] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York (1940), p. 217 ff.

Pauling's argument may be summarized as follows. The conjugated double bond system in diphenyl causes the central C−C bond between the two benzene rings to have partial double bond character. As a consequence the molecule tends to remain coplanar. However, because of the small double-bond character of approximately 20 percent, the force which tends to cause coplanarity is not great. The steric repulsion between overlapping hydrogen atoms located in the adjoining benzene rings may cause the molecule to twist. Moreover, the molecule 1,3,5 triphenyl benzene which would be expected to have steric interaction of the same order of magnitude as diphenyl has been reported to be non-planar. Thus, according to Pauling, the possibility exists on theoretical grounds that the molecule is not planar. The extent to which the planarity assumption is valid will be indicated by the results of the computation, since considerable deviation of the diphenyl molecule from a flat structure would seriously influence the accuracy of the calculation.

II. SYMMETRY OF THE DIPHENYL MOLECULE

The molecule diphenyl belongs to the symmetry[8] point group D_{2h}. The group D_{2h} is a dihedral group which has three mutually perpendicular twofold axes of symmetry (Fig. 1): C_2^x, C_2^y, and C_2^z; and three mutually perpendicular planes of symmetry: σ_h the plane of the molecule, σ_v^x, and σ_v^y, normal to the C_2^x and C_2^y axes, respectively. These 6 symmetry operations together with the identity operation E and inversion operation I form the complete D_{2h} group. The irreducible representations which specify the symmetry of the group D_{2h} are given in Table I.

TABLE I. Character table for group D_{2h}.

	E	C_2^z	C_2^y	C_2^x	I	σ_h	σ_v^y	σ_v^z
$\Gamma_1^D(A_{1g}^D)$	1	1	1	1	1	1	1	1
$\Gamma_2^D(B_{1g}^D)$	1	−1	−1	1	1	−1	−1	1
$\Gamma_3^D(A_{2g}^D)$	1	1	−1	−1	1	1	−1	−1
$\Gamma_4^D(B_{2g}^D)$	1	−1	1	−1	1	−1	1	−1
$\Gamma_5^D(A_{1u}^D)$	1	1	1	1	−1	−1	−1	−1
$\Gamma_6^D(B_{1u}^D)$	1	−1	−1	1	−1	1	1	−1
$\Gamma_7^D(A_{2u}^D)$	1	1	−1	−1	−1	−1	1	1
$\Gamma_8^D(B_{2u}^D)$	1	−1	1	−1	−1	1	−1	1

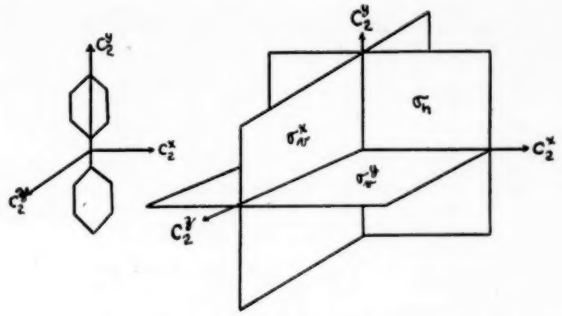

FIG. 1. Symmetry axes and symmetry planes of diphenyl.

In Table I, the irreducible representations are represented by the Γ's in which the superscript D identifies the representation as belonging to diphenyl thus differentiating this set of Γ's from the Γ's used by Wilson[9] in discussing the benzene case. The A's and B's in parentheses are the equivalent symbols in the notation of Mulliken and Placzek.[10]

There are 66 degrees of freedom in the molecule which are distributed among the symmetry groups according to the equation,

$$\Gamma^D = 11\Gamma_1^D + 7\Gamma_2^D + 11\Gamma_3^D + 4\Gamma_4^D + 4\Gamma_5^D + 11\Gamma_6^D + 7\Gamma_7^D + 11\Gamma_8^D, \quad (1)$$

where Γ^D represents the reducible representation of the whole molecule. Of the 66 modes given by Eq. (1), only 60 are vibrational modes, since 6 of the coordinates are required to give the rotation and translation of the molecule as a whole. The Γ^D's corresponding to the "modes" belonging to rotation and translation of the molecule as a whole may be obtained by the following considerations. For the translation "modes" find the symmetry of the deformation pattern for the molecule when all atoms have a displacement in the x direction, corresponding to the x coordinate of translation for the molecule, and similarly for the y and z coordinates. In the case of the rotational coordinates, say rotation about the z axis, the deformation pattern is one in which all of the atoms have a displacement tangential to a circle drawn in the plane of the molecule about the center of symmetry of the

[8] J. Rosenthal and G. Murphy, Rev. Mod. Phys. **8**, 317 (1936).

[9] E. Bright Wilson, Jr., Phys. Rev. **45**, 706 (1934).

[10] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

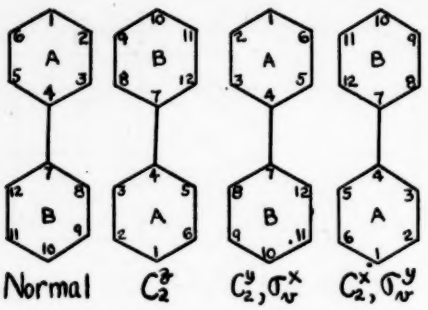

FIG. 2. Effect of symmetry operations on locations of atoms.

molecule. Thus, Table II gives the irreducible representations to which belong the normal coordinates Q_z^T, Q_y^T, Q_x^T, Q_z^ω, Q_y^ω, Q_x^ω where the superscript T and ω represent translation in the direction of, and rotation about the given axes, respectively. Hence, the symmetry of the vibrational modes of diphenyl, Γ_V^D, becomes

$$\Gamma_V^D = 11\Gamma_1^D + 6\Gamma_2^D + 10\Gamma_3^D + 3\Gamma_4^D + 4\Gamma_5^D + 10\Gamma_6^D + 6\Gamma_7^D + 10\Gamma_8^D. \quad (2)$$

Equation (2) tells us that there are 11 normal coordinates having the symmetry Γ_1^D, 6 normal coordinates having the symmetry Γ_2^D, etc. In contradistinction to benzene none of the frequencies is degenerate, since the characters are equal to ± 1 for all Γ^D's. Whereas in benzene there are present 20 different vibrational frequencies, 10 of which are doubly degenerate, in diphenyl, the addition of another benzene ring has produced a new molecule of a lower order of symmetry such that there are no longer present degenerate frequencies. There are 60 different frequencies which must be computed. The group theory is of assistance here in that from (2) we can tell in advance the extent to which the secular determinant for the normal modes is factored. Thus, the 60th-order determinant factors into one 11th-order determinant, three different 10th-order determinants; two 6th-order determinants, one 4th-order determinant, and one 3rd-order determinant.

III. THE DIPHENYL MOLECULAR ORBITALS

In formulating the wave functions to be used to obtain the electronic energy levels of diphenyl one may set up functions which are appropriate products of the one-electron orbitals of benzene given by Hückel,[11] as,

$$\phi_l(\nu) = (6\sigma_l)^{-\frac{1}{2}} \sum_{k=0}^{5} \exp^{2\pi i l k/6} K(\nu). \quad (3)$$

In the above, K represents the $2p\pi$ wave function for the $(1+k)$th carbon atom, where K takes on the values I, II, $\cdots$, VI while k has the corresponding values 0, 1, $\cdots$, 5 for the benzene case. The 6 carbon electrons which give benzene its aromatic properties[1] (GMS) are represented by small Greek letters such as ν, μ, and numerically assume the values 1, 2, $\cdots$, 6 in benzene. Again l may assume the values $l=0$, ± 1, ± 2, 3 corresponding to different one-electron benzene orbitals. The coefficients σ_l are normalization coefficients.

The starting point for setting up the diphenyl orbitals is the consideration that diphenyl consists essentially of two benzene rings. Thus, there are now twelve $2p\pi$ electrons to consider and it is evident that if there were no interaction between rings the energy levels for diphenyl would be the same as those for benzene but they would now each be doubly degenerate. However, since there does exist an electronic interaction between rings the problem becomes equivalent to a perturbation calculation in which, in order to find the perturbation energy, it is convenient to average the interaction energy function over the unperturbed state of the molecule, thus necessitating a determination of the unperturbed wave function. This unperturbed function can be taken as a linear combination of the molecular benzene functions (for the two different rings) which belong to the same energy level. The linear combinations, in addition, should satisfy the condition that they have the same symmetry as diphenyl. That is, the transformation properties of the combination wave functions under the action of the symmetry operations of the point group D_{2h} must be such that each one of the unperturbed functions may

TABLE II. Symmetry of the translational and rotational normal coordinates.

Q_z^T	Q_y^T	Q_x^T	Q_z^ω	Q_y^ω	Q_x^ω
Γ_7^D	Γ_8^D	Γ_6^D	Γ_3^D	Γ_4^D	Γ_2^D

[11] E. Hückel, Zeits. f. Physik **70**, 204 (1931).

be identified with some one of the eight irreducible representations given in Table I.

There are a number of possible methods which may be used in setting up the unperturbed wave function. A straight-forward procedure, analagous to that used by Goeppert-Mayer and Sklar for benzene, may be used in which the linear combinations are made up of twelve-fold sums and differences of one-electron benzene orbitals belonging to the two different benzene rings, ring A and ring B, Fig. 2. The orbital for the state of the entire molecule consists of products of these combined one-electron orbitals.

Another method consists in first setting up linear combinations of the benzene molecular functions which have the benzene symmetry Γ_1, Γ_9, Γ_{10}, and Γ_{12} and which have been found to be the correct functions to use in the calculation of the benzene energy levels. These benzene functions are:

$$\left.\begin{aligned} &\Gamma_1(A_{1g}) \quad \Psi_0=\psi_0,\\ &\Gamma_9(B_{1u}) \quad \Psi_1=2^{-\frac{1}{2}}(\psi_1+\psi_2),\\ &\Gamma_{10}(B_{2u}) \quad \Psi_2=2^{-\frac{1}{2}}(\psi_1-\psi_2),\\ &\Gamma_{12}(E_{1u}) \quad \psi_3,\ \psi_4; \end{aligned}\right\} \tag{4}$$

where

$$\left.\begin{aligned} \psi_0&=\phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-1}(6),\\ \psi_1&=\phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_2(6),\\ \psi_2&=\phi_0(1)\phi_0(2)\phi_{-1}(3)\phi_{-1}(4)\phi_1(5)\phi_{-2}(6),\\ \psi_3&=\phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-2}(6),\\ \psi_4&=\phi_0(1)\phi_0(2)\phi_{-1}(3)\phi_{-1}(4)\phi_1(5)\phi_2(6);\\ &\psi_1=\psi_2^*;\quad \psi_3=\psi_4^*. \end{aligned}\right\} \tag{5}$$

For diphenyl, we will use the functions

$$\left.\begin{aligned} &\Gamma_9(B_{1u}) \quad \Psi_3=2^{-\frac{1}{2}}(\psi_3+\psi_4),\\ &\Gamma_{10}(B_{2u}) \quad \Psi_4=2^{-\frac{1}{2}}(\psi_3-\psi_4), \end{aligned}\right\} \tag{6}$$

which are analagous to Ψ_1, and Ψ_2, instead of ψ_3 and ψ_4.

Taking linear combinations of the benzene functions given in Eqs. (4) and (6) as the unperturbed functions of diphenyl makes possible the treatment of the diphenyl energy levels as perturbed benzene energy levels, and the calculation then makes full use of the previous calculations for benzene. Furthermore, the secular determinant is not as unwieldy as in the first method, for in this case it is automatically factored into quadratic terms from which may be obtained the splitting of each single benzene energy level into the two corresponding diphenyl levels.

The correct diphenyl functions and the irreducible representations to which they belong are then:

$$\left.\begin{aligned} \Psi_0^D&=\Psi_{0A}\Psi_{0B} && \Gamma_1^D,\\ \Psi_1^D&=2^{-\frac{1}{2}}\{\Psi_{0A}\Psi_{1B}+\Psi_{1A}\Psi_{0B}\} && \Gamma_8^D,\\ \Psi_{-1}^D&=2^{-\frac{1}{2}}\{\Psi_{0A}\Psi_{1B}-\Psi_{1A}\Psi_{0B}\} && \Gamma_1^D,\\ \Psi_2^D&=2^{-\frac{1}{2}}\{\Psi_{0A}\Psi_{2B}+\Psi_{2A}\Psi_{0B}\} && \Gamma_6^D,\\ \Psi_{-2}^D&=2^{-\frac{1}{2}}\{\Psi_{0A}\Psi_{2B}-\Psi_{2A}\Psi_{0B}\} && \Gamma_3^D,\\ \Psi_3^D&=2^{-\frac{1}{2}}\{\Psi_{0A}\Psi_{3B}+\Psi_{3A}\Psi_{0B}\} && \Gamma_8^D,\\ \Psi_{-3}^D&=2^{-\frac{1}{2}}\{\Psi_{0A}\Psi_{3B}-\Psi_{3A}\Psi_{0B}\} && \Gamma_1^D,\\ \Psi_4^D&=2^{-\frac{1}{2}}\{\Psi_{0A}\Psi_{4B}+\Psi_{4A}\Psi_{0B}\} && \Gamma_6^D,\\ \Psi_{-4}^D&=2^{-\frac{1}{2}}\{\Psi_{0A}\Psi_{4B}-\Psi_{4A}\Psi_{0B}\} && \Gamma_3^D. \end{aligned}\right\} \tag{7}$$

In the above, the superscript D identifies the diphenyl functions, while the function Ψ_{lA} ($l=1, \cdots, 4$) is the benzene orbital defined in (4) and (6) for ring A, i.e., it is a function of electrons 1 to 6. Similarly Ψ_{lB} is the benzene orbital for ring B, i.e., it is a function of electrons 7 to 12. The function Ψ_{0A} is that for the ground state of benzene so that Ψ_0^D is the molecular orbital for the ground state of diphenyl.

A study of Eqs. (7) will indicate the manner in which they have been set up and also their significance. Thus, the function for the ground state of diphenyl, Ψ_0^D, is one in which benzene ring A is in the ground state and similarly for benzene ring B. A function like Ψ_1^D represents a state of the molecule in which one-half of the time ring A is in the ground state while ring B is in the Ψ_1 state, and the other half of the time ring A is in the Ψ_1 state while ring B is in the ground state. The unperturbed molecular orbitals for diphenyl are thus written as products of two benzene orbitals, one for ring A and one for ring B. Taking linear combinations of the molecular orbitals belonging to the same energy, you obtain the unperturbed wave functions. It will be noted that these functions correspond to the lower energy levels, since only singly excited benzene rings are involved, that is, one of the rings always is in the ground state and no more than one electron is excited.

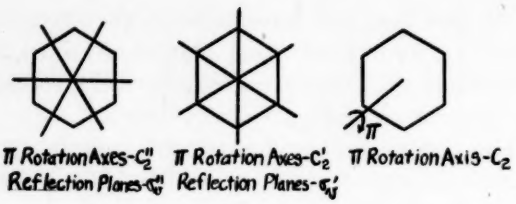

FIG. 3. Some symmetry elements for benzene.

IV. SELECTION RULES

In determining the symmetry of the wave functions it is only necessary to consider the effect of performing the various symmetry operations on the functions. Since benzene functions are involved we shall need to use the character table[9] for the point group D_{6h} to which benzene belongs. Thus, the operation C_2^z on Ψ_1^D may be expressed symbolically as

$$C_2^z\Psi_1^D=\frac{1}{\sqrt{2}}\{(C_2^z\Psi_{0A})(C_2^z\Psi_{1B})+(C_2^z\Psi_{1A})(C_2^z\Psi_{0B})\}. \quad (8)$$

Reference to Fig. 2 shows that the operation C_2^z is equivalent to an interchange of ring A with ring B in the normal arrangement of the molecule followed by the rotation of each benzene ring by the amount π about its own center of symmetry, i.e., the operation C_2 (Fig. 3). Thus, (8) becomes:

$$C_2^z\Psi_1^D=\frac{1}{\sqrt{2}}\{(C_2\Psi_{0B})(C_2\Psi_{1A})+(C_2\Psi_{1B})(C_2\Psi_{0A})\}. \quad (9)$$

Since the function Ψ_0 is symmetric to all symmetry operations in the benzene group, we have $C_2\Psi_{0B}=\Psi_{0B}$ and $C_2\Psi_{0A}=\Psi_{0A}$. Furthermore, since Ψ_{1A} and Ψ_{1B} have the symmetry Γ_9, reference to the character (χ) table given by Wilson[9] shows that $\chi(C_2)=-1$, so that $C_2\Psi_{1A}=-\Psi_{1A}$ or (9) becomes

$$C_2^z\Psi_1^D=\frac{1}{\sqrt{2}}\{(\Psi_{0B})(-\Psi_{1A})+(-\Psi_{1B})(\Psi_{0A})\},$$

or

$$C_2^z\Psi_1^D=-\Psi_1^D. \quad (10)$$

Proceeding in a similar manner with the other symmetry operations one can tabulate the results for Ψ_1^D

	E	C_2^z	C_2^y	C_2^x	I	σ_h	σ_v^y	σ_v^x
Ψ_1^D	1	−1	1	−1	−1	1	−1	1

where the numbers ±1, are the characters for the transformations which result when the symmetry operations are performed on Ψ_1^D. Comparison of the above with Table I shows that Ψ_1^D has the symmetry Γ_8^D. Proceeding in a similar fashion, it is possible to derive the symmetry of the other Ψ^D functions as the following:

$$\left.\begin{aligned}&\Psi_3^D \subset \Psi_1^D \subset \Gamma_8^D,\\ &\Psi_{-3}^D \subset \Psi_{-1}^D \subset \Gamma_1^D,\\ &\Psi_4^D \subset \Psi_2^D \subset \Gamma_6^D,\\ &\Psi_{-4}^D \subset \Psi_{-2}^D \subset \Gamma_3^D.\end{aligned}\right\} \quad (11)$$

Having established the symmetry of the functions given in Eq. (7) it is now possible to determine the selection rules for the electronic transitions.

The three components of the dipole moment of the molecule P_x^D, P_y^D, and P_z^D evidently have the symmetry properties—$P_x^D \subset \Gamma_6^D$, $P_y^D \subset \Gamma_8^D$, $P_z^D \subset \Gamma_7^D$, since the dipole moments have the same symmetry as the translation coordinates given in Table II.

The probability of an electronic transition between the ground state and any excited state, Ψ_l^D, is governed by the integral

$$\int \Psi_l^{D*} P_C^D \Psi_0^D d\tau$$

where P_C^D is any one of the components of the dipole moment P^D. Since, if this integral is to be different from zero, it must remain invariant to any of the group operations, it follows that the equivalent group theoretical statement is that the integral must be totally symmetric; that is, the integral must transform like the irreducible representation Γ_1^D. As $\Psi_0^D \subset \Gamma_1^D$ it is necessary that $P_C^D \times \Psi_7^D \subset \Gamma_1^D$ to satisfy the condition of invariance. Thus, the allowed electronic transi-

TABLE III. Symmetry of vibrations which make forbidden transitions allowed.

Electronic Symmetry	$P_x^D(\Gamma_6^D)$	$P_y^D(\Gamma_8^D)$	$P_z^D(\Gamma_7^D)$
$\Gamma_8^D(\overset{D}{\Psi}_{1,3})$	Γ_3^D	Allowed	Γ_2^D
$\Gamma_1^D(\overset{D}{\Psi}_{-1,-3})$	Γ_6^D	Γ_8^D	Γ_7^D
$\Gamma_6^D(\overset{D}{\Psi}_{2,4})$	Allowed	Γ_3^D	Γ_4^D
$\Gamma_3^D(\overset{D}{\Psi}_{-2,-4})$	Γ_8^D	Γ_6^D	Γ_5^D

tions for P_x^D are those in which the excited state has Γ_6^D symmetry, while for P_y^D the excited state must have Γ_8^D symmetry. P_z^D transitions are not allowed. Transitions involving the functions Ψ_2^D, and Ψ_4^D result in radiation polarized in the x direction, while transitions involving the functions Ψ_1^D and Ψ_3^D result in radiation polarized in the y direction.

However, the possibility exists of weak electronic transitions to states involving $\Psi_{-|l|}^D$ having the symmetry Γ_1^D and Γ_3^D and also to states involving Γ_6^D and Γ_8^D but having different polarization characteristics. All that would be required is that the transition occur to a vibrational level in the excited electronic state such that

$$\Gamma_{P_C^D}^D \Gamma_{V^D} \Gamma_{l^D} = \Gamma_1^D$$

where Γ_V^D is the irreducible representation for the vibrational level. It will be recalled that the Γ_{10} level of 5.0 ev in benzene is a forbidden transition of this kind. As indicated in Table III, which gives the symmetry of the vibrational level which is required to make possible the forbidden transitions to the given electronic level, it is evident that these forbidden levels may appear weakly in the band spectrum since the vibrational modes of diphenyl include all of the Γ^D's (Eq. (2)).

V. ANTISYMMETRIZATION OF THE ORBITALS

Since the electrons in the various orbitals can be in one of two spin states, α or β, and since no two electrons in the same orbital can have the same spin, it is necessary to include an appropriate spin function as a factor to the orbitals (7). For the ground state the spin function is

$$\chi_0^D = \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6)\alpha(7)\beta(8)\alpha(9)\beta(10)\alpha(11)\beta(12). \quad (12)$$

The ground state function must be made antisymmetrical to the interchange of any two electrons and is therefore taken as

$$\Phi_0^D = \frac{1}{(12!N_0)^{\frac{1}{2}}} \sum_P (-1)^P P \Psi_0^D \chi_0^D, \quad (13)$$

where P is any one of the 12! possible permutations of the electrons. Derivation of the normalization factor N_0 is given in Sections VII and VIII below.

For the excited states, only singlet energy levels will be considered. We are mainly interested in the perturbation of the benzene singlet levels since the triplet states of benzene give bands too weak to be observed. The singlet excited state spin function for electrons 1 to 6 is

$$\chi_{SA} = [1/\sqrt{2}]\alpha(1)\beta(2)\alpha(3)\beta(4) \times [\alpha(5)\beta(6) - \beta(5)\alpha(6)]. \quad (14)$$

The appropriate spin function for any one of the excited states, say Ψ_1^D, is obtained by considering each of the two terms which constitute Ψ_1^D separately. Since in a term such as $\Psi_{0A}\Psi_{1B}$ the molecule is partially in the ground state and partially in the excited state Ψ_1, the spin function is correspondingly partially ground state and partially of the nature of (14), i.e., the spin factor is $\chi_{0A}\chi_{SB}$, where χ_{0A} is analogous to (12) with the exception that it is a function of electrons 1 to 6 only.

Accordingly, the totally antisymmetric orbital for Ψ_1^D is

$$\Phi_1^D = \frac{1}{(2 \cdot 12!N_1)^{\frac{1}{2}}} \sum_P (-1)^P P \times \{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB} + \Psi_{1A}\Psi_{0B}\chi_{SA}\chi_{0B}\}, \quad (15)$$

where N_1 again is a normalization factor deduced in Sections VII and VIII. Equation (15) can be shown to be equivalent to a product of coordinate function Ψ_1^D and the singlet spin function for the entire diphenyl molecule. Thus, consider the term

$$\sum_P (-1)^P P\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}\}.$$

It is evident that since the permutations of the 12 electrons form a group it is possible to perform any additional permutation on all members of the group without changing the group. Suppose the permutation $\bar{P}$ is performed where $\bar{P}$ con-

sists in interchanging electrons 5 and 6. Then,

$$\begin{aligned}\sum_P (-1)^P P\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}\} &= -\bar{P}\sum_P (-1)^P P\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}\} \\ &= \sum_P (-1)^{P+1} P[\bar{P}\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}\}] \\ &= -\sum_P (-1)^P P\{\Psi_{0A}\Psi_{1B}(\bar{P}\chi_{0A})\chi_{SB}\} \quad (16)\end{aligned}$$

inasmuch as, only Ψ_{0A} and χ_{0A} can be affected by the permutation $\bar{P}$ of the electrons 5 and 6, while Ψ_{0A} remains unchanged since electrons 5 and 6 are in the same one-electron orbital. In the above

$$\bar{P}\chi_{0A}=\alpha(1)\beta(2)\alpha(3)\beta(4)\beta(5)\alpha(6).$$

Thus,

$$\begin{aligned}2\sum_P (-1)^P P\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}\} &= \sum_P (-1)^P P\{\Psi_{0A}\Psi_{1B}(\chi_{0A}-\bar{P}\chi_{0A})\chi_{SB}\} \\ &= \sum_P (-1)^P P\{\Psi_{0A}\Psi_{1B}(\sqrt{2}\chi_{SA})\chi_{SB}\}. \quad (17)\end{aligned}$$

Equation (15) then becomes

$$\Phi_1{}^D=\frac{1}{(2\cdot 12!N_1)^{\frac{1}{2}}}\sum_P (-1)^P P\Psi_1{}^D\chi_S{}^D, \quad (18)$$

where

$$\chi_S{}^D=\chi_{SA}\chi_{SB}.$$

The antisymmetric orbitals for the other 7 excited functions are exactly analogous to (15).

VI. THE SECULAR DETERMINANT

In setting up the Hamiltonian for diphenyl an extension of the method employed in the benzene case will be used. In the latter method, the interaction energy between the six carbon atoms is divided into two parts consisting of (1), the mutual electronic interaction energy between the six $2p\pi$ electrons, and (2) the potential energy of the $2p\pi$ electrons in the field of the 6 carbon atoms stripped of their $2p\pi$ electrons. The complete Hamiltonian function for the electronic energy of benzene, H, was taken as

$$H=T+H_0+H^e, \quad (19)$$

where T is the kinetic energy operator for the 6 electrons, i.e.,

$$T=-\frac{h^2}{8\pi^2}\sum_{i=1}^{6}\frac{1}{m_i}\nabla_i^2,$$

∇_i^2 being the Laplacian operator for the ith electron; H_0 is the potential energy operator which is equal to $\sum_{K=1}^{6} H_K$, H_K being the potential energy due to the Kth $2p\pi$-stripped carbon atom; and where

$$H^e=\sum_{\substack{\nu=1\\ \mu<\nu}}^{6} e^2/r_{\nu\mu},$$

the electronic interaction. The superscript e will be used to indicate electronic repulsion energy terms.

For diphenyl, the kinetic energy term is expanded to T_A+T_B, since both rings A and B are involved; the electronic interaction term becomes

$$H_D{}^e=\sum_{\substack{\nu=1\\ \mu<\nu}}^{12} e^2/r_{\nu\mu}$$

corresponding to the mutual interaction between the twelve $2p\pi$ electrons; while the potential energy term becomes $\mathcal{H}_{0A}+\mathcal{H}_{0B}$, where $\mathcal{H}_{0A}$ differs from H_{0A} by an additional term designated as $H_{0A}{}^B$ corresponding to the fact that the $2p\pi$ electrons in ring B are now in the field due to ring A, i.e., $\mathcal{H}_{0A}=H_{0A}+H_{0A}{}^B$ and $\mathcal{H}_{0B}=H_{0B}+H_{0B}{}^A$. To all of the above terms must be added a term $H_D{}^I$ which is the mutual interaction energy for the 12 carbon "ions," i.e., the $2p\pi$-less carbon atoms. Since the latter term is not a function of the $2p\pi$ electrons' coordinates, it does not vary with energy level and hence is only of importance in determining the energy of the ground state; the analogous term was not considered in the benzene case for the reason that Goeppert-Mayer and Sklar were not directly concerned with the ground state energy. Similarly $H_D{}^I$ will not be considered here. Accordingly, the Hamiltonian for diphenyl, H^D, becomes

$$H^D=T_A+T_B+\mathcal{H}_{0A}+\mathcal{H}_{0B}+H_D{}^e+H_D{}^I. \quad (20)$$

The energy levels W, then are solutions of the secular determinant (23) where

$$H_{ij}=\int \Phi_i{}^{D*}H^D\Phi_j{}^D d\tau, \quad i=j \text{ or } i\neq j, \quad (21)$$

and

$$N_{ij}=\int \Phi_i{}^{D*}\Phi_j{}^D d\tau, \quad i\neq j. \quad (22)$$

For $i=j$, $N_{ii}=1$ since the Φ^D's have been normalized as in (15).

$$\begin{vmatrix} H_{11}-W & H_{13}-N_{13}W & & & & & & \\ H_{13}-N_{13}W & H_{33}-W & & & & & & \\ & & H_{22}-W & H_{24}-N_{24}W & & & & \\ & & H_{24}-N_{24}W & H_{44}-W & & & & \\ & & & & H_{-1-1}-W & H_{-1-3}-N_{-1-3}W & & \\ & & & & H_{-1-3}-N_{-1-3}W & H_{-3-3}-W & & \\ & & & & & & H_{-2-2}-W & H_{-2-4}-N_{-2-4}W \\ & & & & & & H_{-2-4}-N_{-2-4}W & H_{-4-4}-W \end{vmatrix} = 0. \quad (23)$$

Terms not appearing in (23) are excluded since only interactions between states of the same symmetry do not vanish. This statement is immediately evident since any energy integral must be invariant with respect to any operation in the symmetry group D_{2h}; the H_{ij} integrals transform like $\Psi_i^D \times \Psi_j^D$, which are totally symmetric when both Ψ_i^D and Ψ_j^D belong to the same Γ^D. The functions Φ_i^D are not quite mutually orthogonal, hence, the appearance of the orthogonality integrals N_{ij}, which are evaluated in Sections VII and VIII. However, the Φ_i^D's are normalized so that the coefficient of the W's appearing along the diagonal of the determinant is unity. The integrals H_{ij} and N_{ij} are real as will be demonstrated later.

Expansion of (23) leads to four quadratic equations each one of which determines two energy levels, given by the expression

$$W_{ij}^{\pm} = \frac{1}{1-N_{ij}^2}\left[\frac{H_{ii}+H_{jj}}{2} - N_{ij}H_{ij} \pm \tfrac{1}{2}\left\{(H_{ii}-H_{jj})^2+4H_{ij}^2+4N_{ij}\left[N_{ij}-H_{ij}\left(\frac{1}{H_{ii}}+\frac{1}{H_{jj}}\right)\right]H_{ii}H_{jj}\right\}^{\frac{1}{2}}\right]. \quad (24)$$

Evidently this relatively simple solution of the eighth order determinant (23) results from our choice of the diphenyl functions as linear combinations of the benzene functions. Examination of (24) shows that if the interaction energy H_{ij} is zero, and if the ith and jth functions are mutually orthogonal, i.e., $N_{ij}=0$, the two levels given by (24) are H_{ii} and H_{jj}.

VII. EVALUATION OF H_{ij} AND N_{ij}

It is convenient to separate the H_{ij} integrals into two individual integrals, the electronic interaction energy integral defined as

$$H_{ij}^{e} = \int \Phi_i^{D*} H_D^{e} \Phi_j^D d\tau, \quad (25)$$

and the so-called nuclear interaction energy integral defined as

$$H_{ij}^{n} = \int \Phi_i^{D*}[T_A+T_B+\mathcal{H}_{0A}+\mathcal{H}_{0B}]\Phi_j^D d\tau. \quad (26)$$

Evidently the latter integral represents the interaction energy between the $2p\pi$-less carbon atoms (or "nucleii") and the $2p\pi$ electrons. The superscript n will be used for "nuclear" [12] interaction energy integrals.

[12] It should be noted here that the "nuclear" interaction energy integrals also include kinetic energy terms; in fact, include everything but the electronic interaction energy terms.

The normalization integrals N_{ii}, from which are determined the value of the normalization factors, N_i, and the orthogonality integrals N_{ij} are similar in form to the H_{ii} and H_{ij} integrals, respectively, as may be readily seen by replacing the Hamiltonian operation H^D with the operator *1*.

The evaluation of all of these integrals may be considerably simplified as a result of symmetry considerations.

To exemplify the method involved we carry it out for $i=j=1$. Let $Q_{11}(\theta)$ be one of the three integrals H_{11}^e, H_{11}^n, or N_{11}. Which of the three it is depends on whether the operator θ is

$$H_D^e, \quad [T_A+T_B+\mathcal{H}_{0A}+\mathcal{H}_{0B}], \quad \text{or} \quad 1.$$

Then

$$Q_{11}(\theta)=\int \Phi_1^{D*}\theta\Phi_1^D d\tau. \tag{27}$$

Substituting from Eq. (15) for Φ_1^D we get

$$Q_{11}(\theta)=\frac{1}{2\cdot 12!N_1}\int \sum_{P'}(-1)^{P'}\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}+\Psi_{1A}\Psi_{0B}\chi_{SA}\chi_{0B}\}^*\theta \times\sum_P(-1)^P P\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}+\Psi_{1A}\Psi_{0B}\chi_{SA}\chi_{0B}\}d\tau. \tag{28}$$

This integral may be simplified[13] in the usual manner and (28) may be written as

$$Q_{11}(\theta)=\frac{1}{2N_1}\sum_P(-1)^P\int\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}+\Psi_{1A}\Psi_{0B}\chi_{SA}\chi_{0B}\}^*\theta P\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}+\Psi_{1A}\Psi_{0B}\chi_{SA}\chi_{0B}\}d\tau. \tag{29}$$

Evidently $Q_{11}(\theta)=1$ for $\theta=1$ from the definition of N_1. Equation (29) may be written as four integrals, i.e.,

$$Q_{11}(\theta)=\frac{1}{N_1}[{}_aQ_{11}(\theta)+{}_bQ_{11}(\theta)+{}_cQ_{11}(\theta)+{}_dQ_{11}(\theta)], \tag{30}$$

where

$$\left.\begin{aligned}
{}_aQ_{11}(\theta)&=\tfrac{1}{2}\sum_P(-1)^P\int\{\Psi_{0A}^*\Psi_{1B}^*\chi_{0A}\chi_{SB}\}\theta P\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}\}d\tau,\\
{}_bQ_{11}(\theta)&=\tfrac{1}{2}\sum_P(-1)^P\int\{\Psi_{0A}^*\Psi_{1B}^*\chi_{0A}\chi_{SB}\}\theta P\{\Psi_{1A}\Psi_{0B}\chi_{SA}\chi_{0B}\}d\tau,\\
{}_cQ_{11}(\theta)&=\tfrac{1}{2}\sum_P(-1)^P\int\{\Psi_{1A}^*\Psi_{0B}^*\chi_{SA}\chi_{0B}\}\theta P\{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}\}d\tau,\\
{}_dQ_{11}(\theta)&=\tfrac{1}{2}\sum_P(-1)^P\int\{\Psi_{1A}^*\Psi_{0B}^*\chi_{SA}\chi_{0B}\}\theta P\{\Psi_{1A}\Psi_{0B}\chi_{SA}\chi_{0B}\}d\tau.
\end{aligned}\right\} \tag{31}$$

It may be readily demonstrated that

$${}_aQ_{11}(\theta)={}_dQ_{11}(\theta), \quad {}_bQ_{11}(\theta)={}_cQ_{11}(\theta). \tag{32}$$

Thus θ is unaltered, irrespective of whether it is H_D^e, $[T_A+T_B+\mathcal{H}_{0A}+\mathcal{H}_{0B}]$, or 1, if we interchange the symbols A and B. This interchange, which immediately changes ${}_aQ_{11}(\theta)$ into ${}_dQ_{11}(\theta)$ and ${}_bQ_{11}(\theta)$ into ${}_cQ_{11}(\theta)$, is permitted since its only effect is to change the name of the integration variables.

The general result follows immediately that

$$\left.\begin{aligned}
{}_aQ_{ii}(\theta)&={}_dQ_{ii}(\theta)\\
{}_bQ_{ii}(\theta)&={}_cQ_{ii}(\theta)
\end{aligned}\right\} i=\pm1, \pm2, \pm3, \pm4, \tag{33}$$

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[13] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), first edition, p. 240.

for ${}_aQ_{ii}(\theta)$ and ${}_bQ_{ii}(\theta)$ are exactly analogous to ${}_aQ_{11}(\theta)$ and ${}_bQ_{11}(\theta)$, respectively, it being possible to obtain the former integrals from the latter by replacing Ψ_{1A} (or Ψ_{1B}) with Ψ_{iA} (or Ψ_{iB} where $i=1, 2, 3, 4$). The proof of (33) is exactly analogous to that given for (32). From the definition of the $\Psi_{-i}{}^D$ functions as given in Eq. (7) it follows that

$$\left.\begin{aligned} {}_aQ_{-i-i}(\theta) &= {}_aQ_{ii}(\theta) \\ {}_bQ_{-i-i}(\theta) &= -{}_bQ_{ii}(\theta) \end{aligned}\right\} i=1, 2, 3, 4. \tag{34}$$

For the next step in the evaluation of $Q_{11}(\theta)$ it is advantageous to consider the case where $\theta=H_D{}^e$. It is possible to split the integral $Q_{11}(H_D{}^e)$ or $H_{11}{}^e$ into two parts, one part of which is due to the benzene electronic interaction in each ring, and the other part of which is due to electronic interaction between rings. Thus let

$$H_D{}^e=\sum_{\substack{\nu=1\\ \mu<\nu}}^{12} e^2/r_{\nu\mu}=\sum_{\substack{\nu=1\\ \mu<\nu}}^{6} e^2/r_{\nu\mu}+\sum_{\substack{\nu=7\\ 7\leq\mu<\nu}}^{12} e^2/r_{\nu\mu}+\sum_{\nu=1}^{6}\sum_{\mu=7}^{12} e^2/r_{\nu\mu} \tag{35}$$

or

$$H_D{}^e= \quad H_A{}^e \quad +H_B{}^e \quad +H_{AB}{}^e. \tag{36}$$

Furthermore, the permutation operator P in Eq. (31) may be subdivided into four different types of permutations, i.e.,

$$P=P_A+P_B+P_{A\cdot B}+P_{AB}, \tag{37}$$

where P_A represents permutations of electrons in the A ring only, and P_B represents permutations of electrons in the B ring only. P_{AB} is a symbol for the following class of permutations: The first permutation of the class matches up as many electrons as possible.[14] The other permutations of P_{AB} are all those permutations which start with the result of the first operation just described and in which at least one of the permuted electron pairs contains one electron in ring A and one electron in ring B. Under the latter definition, permutations also included in P_{AB} are those for which an interchange between electrons in two different rings is concurrent with interchanges confined to electrons located in the same ring. $P_{A\cdot B}$ represents permutations in ring A occurring simultaneously with permutations in ring B, but without any crossing over between rings.

Substituting the values of $H_D{}^e$ and P from Eqs. (36) and (37) into ${}_aH_{11}{}^e$ splits this integral into 12 separate integrals. Fortunately, however, a considerable number of these are zero. If we consider first the integrals arising from $H_A{}^e$, we get for P_A the integral, apart from the normalization factor,

$$\tfrac{1}{2}\sum_{P_A}(-1)^{P_A}\int \Psi_{0A}{}^*\chi_{0A}H_A{}^eP_A\Psi_{0A}\chi_{0A}d\tau_A\int \Psi_{1B}{}^*\chi_{SB}\Psi_{1B}\chi_{SB}d\tau_B. \tag{38}$$

The second integral in (38) is equal to unity, while the first integral, has already been evaluated by Goeppert-Mayer and Sklar (see GMS Eq. (15)) and (38) is equal to $\frac{1}{2}E_0{}^e$ where

$$E_0{}^e=E_0-(2\mathcal{E}_0+4\mathcal{E}_1). \tag{39}$$

For $(P_B, H_A{}^e)$ and $(P_{A\cdot B}, H_A{}^e)$ the integral is zero, permutations confined to ring B not being allowed as a consequence of the orthogonality of the one-electron orbital (including spin functions). This leaves the integral P_{AB}, $H_A{}^e$ to be evaluated.

Similarly, for H_B, the integral is zero for P_A and $P_{A\cdot B}$ while for P_B we obtain

$$\tfrac{1}{2}\sum_{P_B}(-1)^{P_B}\int \Psi_{1B}{}^*\chi_{SB}H_B{}^eP_B\Psi_{1B}\chi_{SB}d\tau_B=\tfrac{1}{2}E_{1S}{}^e=\tfrac{1}{2}[E_{1S}-(2\epsilon_0+3\epsilon_1)], \tag{40}$$

[14] Matching up means that the electron ν occurs in this form: $\cdots\phi_{l_A}{}^*(\nu)\cdots H\cdots\phi_{l_A}(\nu)\cdots$ or $\cdots\phi_{l_B'}(\nu)\cdots H\cdots\times\phi_{l_B'}(\nu)\cdots$.

where E_{1s} is given by GMS, Eq. (16), (see also Eq. (75)). Similarly the integral (P_{AB}, H_B^e) remains to be evaluated.

In the third set of integrals involving H_{AB}^e only permutations of the type P_{AB} are allowed. This follows from the fact that H_{AB}^e is the interaction between one electron in the A ring and one in the B ring, thus making impossible permutations confined to one ring, since all of the one-electron orbitals in the one ring are orthogonal to each other. Accordingly, combining this integral with the other two involving P_{AB} which have been previously mentioned, there results the integral

$$ {}_ah_{11}^e = \tfrac{1}{2} \sum_{P_{AB}} (-1)^{P_{AB}} \int \{\Psi_{0A}^* \Psi_{1B}^* \chi_{0A}\chi_{SB}\} H_D^e P_{AB} \{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}\} d\tau_B, \tag{41} $$

where the lower case letter h^e will be used for integrals involving terms containing only P_{AB} and H_D^e. Thus, we have shown that

$$ {}_aH_{11}^e = \frac{1}{2N_1}(E_0^e + E_{1S}^e) + \frac{1}{N_1} {}_ah_{11}^e. \tag{42} $$

It is readily demonstrated that

$$ {}_bH_{11}^e = \frac{1}{N_1} {}_bh_{11}^e = \frac{1}{2N_1} \sum_{P_{AB}} (-1)^{P_{AB}} \int \{\Psi_{0A}^* \Psi_{1B}^* \chi_{0A}\chi_{SB}\} H_D^e P_{AB} \{\Psi_{1A}\Psi_{0B}\chi_{SA}\chi_{0B}\} d\tau. \tag{43} $$

Equation (43) follows from the fact that the benzene functions Ψ_0 and Ψ_1 are mutually orthogonal. For (P_A, H_A^e) and (P_B, H_A^e) the integral containing the B subscript functions is zero; for (P_A, H_B^e) and (P_B, H_B^e) the integral containing the A subscript functions is zero; similarly the $(P_{A\cdot B}, H_A^e)$ and $(P_{A\cdot B}, H_B^e)$ integrals are zero. For (P_A, H_{AB}^e) the integral is zero since any permutation in the A ring will involve at least one A electron which is not functionally related to H_{AB}^e, thus making the integral vanish because of the orthogonality of the one-electron orbitals (including spin function). Similarly for (P_B, H_{AB}^e) and $(P_{A\cdot B}, H_{AB}^e)$ the integrals vanish.

For the nuclear interaction energy ${}_aH_{11}^n$, little advantage is gained in splitting off at this time the benzene nuclear terms. Also, for the normalization integrals, it is advantageous to retain the more general form. Hence,

$$ {}_aH_{11}(I) = \frac{1}{N_1} {}_aN_{11} = \frac{1}{2N_1} \Sigma_P (-1)^P \int \{\Psi_{0A}^* \Psi_{1B}^* \chi_{0A}\chi_{SB}\} IP \{\Psi_{0A}\Psi_{1B}\chi_{0A}\chi_{SB}\} d\tau. \tag{44} $$

Thus we have to compute the set of integrals ${}_ah_{11}^e$, ${}_aH_{11}^n$, and ${}_aN_{11}$; also ${}_bh_{11}^e$, ${}_bH_{11}^n$, and ${}_bN_{11}$. The two sets of three integrals are somewhat similar in form since the same molecular orbital functions appear in each integral. Each one of these integrals splits into four integrals if the expression given in Eq. (4) is substituted for Ψ_1. The four integrals which are obtained for ${}_ah_{11}^e$ and which are of similar appearance for the other two in the set of integrals represented by the pre-subscript "a" are,

$$ \left.\begin{aligned}
{}_{a_1}h_{11}^e &= \tfrac{1}{4} \sum_{P_{AB}} (-1)^{P_{AB}} \int \{\psi_{0A}^* \psi_{1B}^* \chi_{0A}\chi_{SB}\} H_D^e P_{AB} \{\psi_{0A}\psi_{1B}\chi_{0A}\chi_{SB}\} d\tau, \\
{}_{a_2}h_{11}^e &= \tfrac{1}{4} \sum_{P_{AB}} (-1)^{P_{AB}} \int \{\psi_{0A}^* \psi_{1B}^* \chi_{0A}\chi_{SB}\} H_D^e P_{AB} \{\psi_{0A}\psi_{2B}\chi_{0A}\chi_{SB}\} d\tau, \\
{}_{a_3}h_{11}^e &= \tfrac{1}{4} \sum_{P_{AB}} (-1)^{P_{AB}} \int \{\psi_{0A}^* \psi_{2B}^* \chi_{0A}\chi_{SB}\} H_D^e P_{AB} \{\psi_{0A}\psi_{1B}\chi_{0A}\chi_{SB}\} d\tau, \\
{}_{a_4}h_{11}^e &= \tfrac{1}{4} \sum_{P_{AB}} (-1)^{P_{AB}} \int \{\psi_{0A}^* \psi_{2B}^* \chi_{0A}\chi_{SB}\} H_D^e P_{AB} \{\psi_{0A}\psi_{2B}\chi_{0A}\chi_{SB}\} d\tau.
\end{aligned}\right\} \tag{45} $$

It is now possible to show that

$$ {}_{a_1}h_{11}{}^{e}=({}_{a_4}h_{11}{}^{e})^*, \quad {}_{a_2}h_{11}{}^{e}=({}_{a_3}h_{11}{}^{e})^*, \tag{46} $$

so that

$$ {}_{a}h_{11}{}^{e}=2Re({}_{a_1}h_{11}{}^{e}+{}_{a_2}h_{11}{}^{e}), \tag{47} $$

where *Re* signifies the real part of the expression in parenthesis.

Equation (46) may be proved by taking the complex conjugate of ${}_{a_4}h_{11}{}^{e}$. This changes $\psi_{0A}{}^*\psi_{2B}{}^*$ to $\psi_{0A}\psi_{2B}$ and similarly $\psi_{0A}\psi_{2B}$ becomes $\psi_{0A}{}^*\psi_{2B}{}^*$. Reference to Eq. (5) shows that the integral may be written as follows:

$$ ({}_{a_4}h_{11}{}^{e})^*=\tfrac{1}{4}\sum_{P_{AB}}(-1)^{P_{AB}}\int\{\psi_{0A}\psi_{1B}{}^*\chi_{0A}\chi_{SB}\}H_D{}^{e}P_{AB}\{\psi_{0A}{}^*\psi_{1B}\chi_{0A}\chi_{SB}\}d\tau. \tag{48} $$

However, since $\phi_l{}^*=\phi_{-l}$ the only difference between $\psi_{0A}\chi_{0A}$ and $\psi_{0A}{}^*\chi_{0A}$ is that electrons 3 and 5, 4 and 6 are mutually interchanged. Since the integral (48) would not be affected by such a change in variable designation, $\psi_{0A}{}^*$ may be replaced by ψ_{0A} and *vice versa*, so that Eq. (48) becomes identical with ${}_{a_1}h_{11}{}^{e}$. A similar demonstration suffices to show the equality of ${}_{a_2}h_{11}{}^{e}$ and ${}_{a_3}h_{11}{}^{e*}$.

For ${}_{b}h_{11}{}^{e}$ we similarly get four integrals:

$$ \left.\begin{aligned}
{}_{b_1}h_{11}{}^{e}&=\tfrac{1}{4}\sum_{P_{AB}}(-1)^{P_{AB}}\int\{\psi_{0A}{}^*\psi_{1B}{}^*\chi_{0A}\chi_{SB}\}H_D{}^{e}P_{AB}\{\psi_{1A}\psi_{0B}\chi_{SA}\chi_{0B}\}d\tau,\\
{}_{b_2}h_{11}{}^{e}&=\tfrac{1}{4}\sum_{P_{AB}}(-1)^{P_{AB}}\int\{\psi_{0A}{}^*\psi_{1B}{}^*\chi_{0A}\chi_{SB}\}H_D{}^{e}P_{AB}\{\psi_{2A}\psi_{0B}\chi_{SA}\chi_{0B}\}d\tau,\\
{}_{b_3}h_{11}{}^{e}&=\tfrac{1}{4}\sum_{P_{AB}}(-1)^{P_{AB}}\int\{\psi_{0A}{}^*\psi_{2B}{}^*\chi_{0A}\chi_{SB}\}H_D{}^{e}P_{AB}\{\psi_{1A}\psi_{0B}\chi_{SA}\chi_{0B}\}d\tau,\\
{}_{b_4}h_{11}{}^{e}&=\tfrac{1}{4}\sum_{P_{AB}}(-1)^{P_{AB}}\int\{\psi_{0A}{}^*\psi_{2B}{}^*\chi_{0A}\chi_{SB}\}H_D{}^{e}P_{AB}\{\psi_{2A}\psi_{0B}\chi_{SA}\chi_{0B}\}d\tau.
\end{aligned}\right\} \tag{49} $$

It may be shown that

$$ {}_{b_1}h_{11}{}^{e}=({}_{b_4}h_{11}{}^{e})^*, \quad {}_{b_2}h_{11}{}^{e}=({}_{b_3}h_{11}{}^{e})^*, \tag{50} $$

so that

$$ {}_{b}h_{11}{}^{e}=2Re({}_{b_1}h_{11}{}^{e}+{}_{b_2}h_{11}{}^{e}). \tag{51} $$

Equation (50) follows from considerations similar to those given in connection with (46) with the exception that in order to convert ψ_{0A} to $\psi_{0A}{}^*$ in the left-hand parenthesis in the integrand of, say, ${}_{b_4}h_{11}{}^{e*}$, interchange of variable designations $\nu=3$ with $\nu=5$ and 4 with 6 in the entire integral also changes ψ_{2A}. However, it is always possible to regain the original form of ψ_{2A} by performing the inverse double interchange in the parenthesis to the right of P_{AB}, since this is an allowed permutation in P_{AB}, which, furthermore, has no effect on the value of the integral. Similarly, it is possible to convert $\psi_{0B}{}^*$ to ψ_{0B}. The details of this proof are given in Appendix I.

We are now in a position to summarize some of the results obtained in the above. Evidently, we have shown that

$$ H_{11}{}^{e}=\frac{1}{N_1}(E_0{}^{e}+E_{1S}{}^{e})+\frac{4}{N_1}Re({}_{a_1}h_{11}{}^{e}+{}_{a_2}h_{11}{}^{e}+{}_{b_1}h_{11}{}^{e}+{}_{b_2}h_{11}{}^{e}), \tag{52} $$

and that this integral is real. Furthermore, for $H_{11}{}^{n}$ we have

$$ H_{11}{}^{n}=\frac{4}{N_1}Re({}_{a_1}H_{11}{}^{n}+{}_{a_2}H_{11}{}^{n}+{}_{b_1}H_{11}{}^{n}+{}_{b_2}H_{11}{}^{n}), \tag{53} $$

and for $Q_{11}(1)$,

$$ Q_{11}(1)=1=\frac{4}{N_1}Re({}_{a_1}N_{11}+{}_{a_2}N_{11}+{}_{b_1}N_{11}+{}_{b_2}N_{11}). \tag{54} $$

Proceeding in a similar fashion it is possible to obtain the following set of equations for the electronic interaction energy terms:

$$
\begin{aligned}
H_{11}^{e} &= \frac{1}{N_1}(E_0^{e}+E_{1S}^{e})+\frac{4}{N_1}Re[(a_1h_{11}^{e}+a_2h_{11}^{e})+(b_1h_{11}^{e}+b_2h_{11}^{e})],\\
H_{-1-1}^{e} &= \frac{1}{N_{-1}}(E_0^{e}+E_{1S}^{e})+\frac{4}{N_{-1}}Re[(a_1h_{11}^{e}+a_2h_{11}^{e})-(b_1h_{11}^{e}+b_2h_{11}^{e})],\\
H_{22}^{e} &= \frac{1}{N_2}(E_0^{e}+E_{2S}^{e})+\frac{4}{N_2}Re[(a_1h_{11}^{e}-a_2h_{11}^{e})+(b_1h_{11}^{e}-b_2h_{11}^{e})],\\
H_{-2-2}^{e} &= \frac{1}{N_{-2}}(E_0^{e}+E_{2S}^{e})+\frac{4}{N_{-2}}Re[(a_1h_{11}^{e}-a_2h_{11}^{e})-(b_1h_{11}^{e}-b_2h_{11}^{e})],\\
H_{33}^{e} &= \frac{1}{N_3}(E_0^{e}+E_{3S}^{e})+\frac{4}{N_3}Re[(a_1h_{33}^{e}+a_2h_{33}^{e})+(b_1h_{33}^{e}+b_2h_{33}^{e})],\\
H_{-3-3}^{e} &= \frac{1}{N_{-3}}(E_0^{e}+E_{3S}^{e})+\frac{4}{N_{-3}}Re[(a_1h_{33}^{e}+a_2h_{33}^{e})-(b_1h_{33}^{e}+b_2h_{33}^{e})],\\
H_{44}^{e} &= \frac{1}{N_4}(E_0^{e}+E_{3S}^{e})+\frac{4}{N_4}Re[(a_1h_{33}^{e}-a_2h_{33}^{e})+(b_1h_{33}^{e}-b_2h_{33}^{e})],\\
H_{-4-4}^{e} &= \frac{1}{N_{-4}}(E_0^{e}+E_{3S}^{e})+\frac{4}{N_{-4}}Re[(a_1h_{33}^{e}-a_2h_{33}^{e})-(b_1h_{33}^{e}-b_2h_{33}^{e})],
\end{aligned}
\tag{55}
$$

where E_0^{e}, E_{1S}^{e}, E_{2S}^{e}, E_{3S}^{e} are benzene energy terms (see Eq. (75) below).

Evidently the appearance of the minus sign in H_{-1-1}^{e} and the relationship of the latter to H_{11}^{e} is in part a consequence of Eq. (34). The minus signs in H_{22}^{e} follow from the relationship between Ψ_1 and Ψ_2 given in Eq. (4). The four equations in which $i=\pm 3, \pm 4$ follow in a similar fashion from Eqs. (4) and (34). All of these four equations have the common term E_{3S}^{e}, due to the degeneracy of Ψ_3 and Ψ_4. In obtaining the term E_{3S}^{e}, an integral of the form

$$
\tfrac{1}{2}\sum_{P_B}(-1)^{P_B}\int \Psi_{3B}^{*}\chi_{SB}H_B^{e}P_B\Psi_{3B}\chi_{SB}d\tau_B \tag{56}
$$

is involved. Applying Eq. (6), (56) becomes

$$
\begin{aligned}
\tfrac{1}{4}\sum_{P_B}(-1)^{P_B}\Big[&\int \psi_{3B}^{*}\chi_{SB}H_B^{e}P_B\psi_{3B}\chi_{SB}d\tau_B+\int \psi_{3B}^{*}\chi_{SB}H_B^{e}P_B\psi_{4B}\chi_{SB}d\tau_B\\
&+\int \psi_{4B}^{*}\chi_{SB}H_B^{e}P_B\psi_{3B}\chi_{SB}d\tau_B+\int \psi_{4B}^{*}\chi_{SB}H_B^{e}P_B\psi_{4B}\chi_{SB}d\tau_B\Big].
\end{aligned}
\tag{57}
$$

The first and last integrals are equal to E_{3S}^{e}, while the second and third terms lead to integrals

$$
\int \phi_1^{*}(\nu)\phi_{-1}(\nu)H^{e}\phi_{-2}^{*}(\mu)\phi_2(\mu)d\tau \quad \text{and} \quad \int \phi_1^{*}(\nu)\phi_2(\nu)H^{e}\phi_{-2}^{*}(\mu)\phi_{-1}(\mu)d\tau.
$$

Although H^{e} is invariant these integrals are not invariant to a rotation of say $2\pi/6$ about the symmetry axis of benzene, and hence must be equal to zero. A rotation such as $2\pi/6=\omega$ multiplies the first integral by the term $e^{-i\omega}e^{-i\omega}e^{2i\omega}e^{2i\omega}=e^{2i\omega}$ and, the second integral by $e^{-i\omega}e^{2i\omega}e^{2i\omega}e^{-i\omega}=e^{2i\omega}$.

Thus, for the electronic interaction energy only eight separate terms need be evaluated for the H_{ii}^{e} values. Analogous terms containing the same orbital functions in the integrals are required for

the H_{ii}^n and the $H_{ii}(1)$. For each of the latter a set of eight equations similar to (55) may be constructed by analogy from Eqs. (52)–(54). For reference purposes, the eight individual terms required to determine the $Q_{ii}(\theta)$ are written out in Appendix II in terms of the one-electron orbitals and their spin functions.

Next, we consider the evaluation of the H_{ij} terms when $i \neq j$. Four sets of integrals need to be determined, i.e., for the combinations, $(i, j) = (1, 3); (2, 4); (-1, -3); (-2, -4)$. The method is analogous to that used for the Q_{ii} terms. For illustrative purposes, we may consider the case of Q_{13}.

As before, introducing the general operator θ, it is possible to show that

$$Q_{13}(\theta) = \frac{2}{(N_1 N_3)^{\frac{1}{2}}}[{}_aQ_{13}(\theta) + {}_bQ_{13}(\theta)]. \tag{58}$$

Evidently the reason for this is exactly that given in connection with Eq. (33), i.e., $C_2\Psi_1 = -\Psi_1$, and $C_2\Psi_3 = -\Psi_3$. Thus, the general result that

$$Q_{ij}(\theta) = \frac{2}{(N_i N_j)^{\frac{1}{2}}}[{}_aQ_{ij}(\theta) + {}_bQ_{ij}(\theta)] \tag{59}$$

is also true. Furthermore,

$$\left.\begin{aligned} {}_aQ_{-i-j}(\theta) &= {}_aQ_{ij}(\theta) \\ {}_bQ_{-i-j}(\theta) &= -{}_bQ_{ij}(\theta) \end{aligned}\right\} (i, j) = (1, 3); (2, 4). \tag{60}$$

Considering specifically ${}_aH_{13}^e$, it splits into four terms, i.e.,

$${}_aH_{13}^e = \frac{1}{(N_1 N_3)^{\frac{1}{2}}}({}_{a_1}H_{13}^e + {}_{a_2}H_{13}^e + {}_{a_3}H_{13}^e + {}_{a_4}H_{13}^e), \tag{61}$$

where

$$\begin{aligned}
{}_{a_1}H_{13}^e &= \tfrac{1}{4}\textstyle\sum_P (-1)^P \int \{\psi_{0A}^*\psi_{1B}^*\chi_{0A}\chi_{SB}\} H_D^e P\{\psi_{0A}\psi_{3B}\chi_{0A}\chi_{SB}\} d\tau, \\
{}_{a_2}H_{13}^e &= \tfrac{1}{4}\textstyle\sum_P (-1)^P \int \{\psi_{0A}^*\psi_{1B}^*\chi_{0A}\chi_{SB}\} H_D^e P\{\psi_{0A}\psi_{4B}\chi_{0A}\chi_{SB}\} d\tau, \\
{}_{a_3}H_{13}^e &= \tfrac{1}{4}\textstyle\sum_P (-1)^P \int \{\psi_{0A}^*\psi_{2B}^*\chi_{0A}\chi_{SB}\} H_D^e P\{\psi_{0A}\psi_{3B}\chi_{0A}\chi_{SB}\} d\tau, \\
{}_{a_4}H_{13}^e &= \tfrac{1}{4}\textstyle\sum_P (-1)^P \int \{\psi_{0A}^*\psi_{2B}^*\chi_{0A}\chi_{SB}\} H_D^e P\{\psi_{0A}\psi_{4B}\chi_{0A}\chi_{SB}\} d\tau.
\end{aligned} \tag{62}$$

Utilizing Eqs. (46) and (47) in say ${}_{a_1}H_{13}^e$ we see, as discussed after Eq. (43), that the (P_A, H_A^e) integral is zero, since ψ_1 is orthogonal to ψ_3. For (P_B, H_B^e) the integral is zero since it leads to integrals which are not invariant to a rotation of ω about the C_2 axis although H_D^e is invariant (compare discussion in connection with (57)). For the same reason (P_A, H_B^e) is zero, while (P_B, H_A^e) is zero, because of the orthogonality of ψ_1 and ψ_3. The only integrals which remain are those due to (P_{AB}, H_D^e), so that ${}_{a_1}H_{13}^e$ becomes ${}_{a_1}h_{13}^e$. Similarly ${}_{a_2}H_{13}^e = {}_{a_2}h_{13}^e$, ${}_{a_3}H_{13}^e = {}_{a_3}h_{13}^e$, ${}_{a_4}H_{13}^e = {}_{a_4}h_{13}^e$. (See text following Eq. (41) for definition of h^e.) It is also possible to show (compare derivations of (46)) that:

$${}_{a_1}h_{13}^e = ({}_{a_4}h_{13}^e)^*, \quad {}_{a_2}h_{13}^e = ({}_{a_3}h_{13}^e)^*. \tag{63}$$

For ${}_bH_{13}^e$, by an exactly analogous procedure, it turns out that

$${}_bH_{13}^e = \frac{2}{(N_1 N_3)^{\frac{1}{2}}} Re({}_{b_1}h_{13}^e + {}_{b_2}h_{13}^e), \tag{64}$$

where

$$\left.\begin{aligned} {}_{b_1}h_{13}{}^{e}&=\tfrac{1}{4}\sum_{PAB}(-1)^{PAB}\int\{\psi_{0A}{}^{*}\psi_{1B}{}^{*}\chi_{0A}\chi_{SB}\}H_{D}{}^{e}P_{AB}\{\psi_{3A}\psi_{0B}\chi_{SA}\chi_{0B}\}d\tau,\\ {}_{b_2}h_{13}{}^{e}&=\tfrac{1}{4}\sum_{PAB}(-1)^{PAB}\int\{\psi_{0A}{}^{*}\psi_{1B}{}^{*}\chi_{0A}\chi_{SB}\}H_{D}{}^{e}P_{AB}\{\psi_{4A}\psi_{0B}\chi_{SA}\chi_{0B}\}d\tau. \end{aligned}\right\} \tag{65}$$

Thus,

$$H_{13}{}^{e}=\frac{4}{(N_1N_3)^{\frac{1}{2}}}Re(a_1h_{13}{}^{e}+a_2h_{13}{}^{e}+b_1h_{13}{}^{e}+b_2h_{13}{}^{e}). \tag{66}$$

Also

$$H_{13}{}^{n}=\frac{4}{(N_1N_3)^{\frac{1}{2}}}Re(a_1H_{13}{}^{n}+a_2H_{13}{}^{n}+b_1H_{13}{}^{n}+b_2H_{13}{}^{n}), \tag{67}$$

and

$$N_{13}=\frac{4}{(N_1N_3)^{\frac{1}{2}}}Re(a_1N_{13}+a_2N_{13}+b_1N_{13}+b_2N_{13}). \tag{68}$$

Using (60) and the relationship between Ψ_1 and Ψ_2, Ψ_3 and Ψ_4 we get in addition to (66)

$$\left.\begin{aligned} H_{-1-3}{}^{e}&=\frac{4}{(N_{-1}N_{-3})^{\frac{1}{2}}}Re[(a_1h_{13}{}^{e}+a_2h_{13}{}^{e})-(b_1h_{13}{}^{e}+b_2h_{13}{}^{e})],\\ H_{24}{}^{e}&=\frac{4}{(N_2N_4)^{\frac{1}{2}}}Re[(a_1h_{13}{}^{e}-a_2h_{13}{}^{e})+(b_1h_{13}{}^{e}-b_2h_{13}{}^{e})],\\ H_{-2-4}{}^{e}&=\frac{4}{(N_{-2}N_{-4})^{\frac{1}{2}}}Re[(a_1h_{13}{}^{e}-a_2h_{13}{}^{e})-(b_1h_{13}{}^{e}-b_2h_{13}{}^{e})]. \end{aligned}\right\} \tag{69}$$

Similar equations result for $\theta=H_D{}^{n}$ and $\theta=1$ (compare (67) and (68)).

The four $q_{ij}(\theta)$ integrals are written out in terms of the one-electron orbitals in Appendix II, Eq. (2A). The lower case q is used to represent integrals involving the operator θ and its corresponding permutation operator $P(\theta)$.

VIII. THE NORMALIZATION INTEGRALS N_{ii} AND N_{ij}

We next undertake the computation of the integrals N_{ii}, N_{ij} or $Q_{ii}(1)$ and $Q_{ij}(1)$, respectively. Since $N_{ii}=1$, the N_{ii} integrals really define the normalization factors N_i. The procedure involved will be illustrated in the calculation for N_i.

From Eq. (54) it will be seen that we need to evaluate terms such as ${}_{a_1}N_{11}$. Equations (1A) in Appendix II are helpful here since, if in ${}_{a_1}q_{11}(\theta)$ we substitute for the operator the value $\theta=1$ and for $P(\theta)$ the value P, we get an explicit formulation of the integral ${}_{a_1}N_{11}$.

For the identity permutation in which the electrons remain in their originally assigned orbitals, the integral ${}_{a_1}N_{11}$ is equal to $\frac{1}{4}$. The only other permutations which are not zero are those involving an interchange between rings. These result in integrals differing from zero, which represent the extent of overlapping between an one-electron orbital in one ring with another one-electron orbital belonging to the other ring. The diphenyl overlap integrals $\Delta_{l_Al_B'}$ are defined as follows:

$$\Delta_{l_Al_B'}=\int\phi_{l_A}{}^{*}(\nu)\phi_{l_B'}(\nu)d\tau_{\nu}. \tag{70}$$

Their origin can be seen in the specific example of the allowed permutation which interchanges electrons (1) and (7) in ${}_{a_1}N_{11}$. This results in a contribution to the total value of ${}_{a_1}N_{11}$ in the amount of

$$-\frac{1}{4}\left[\int\phi_{0A}{}^{*}(1)\phi_{0B}(1)d\tau_1\right]\left[\int\phi_{0B}{}^{*}(7)\phi_{0A}(7)d\tau_7\right]=-\frac{1}{4}\Delta_{0A0B}\Delta_{0B0A}. \tag{71}$$

A considerable number of Δ integrals arise as a result of the permutations. Hence, it will be convenient to obtain a general expression for $\Delta_{l_A l_B'}$ in order to obtain the numerical values of the various Δ's involved. Substituting from Eq. (3) for ϕ_{l_A} and $\phi_{l_B'}$ there is obtained

$$\Delta_{l_A l_B'}=\frac{1}{6(\sigma_{l_A}\sigma_{l_B'})^{\frac{1}{2}}}\{\exp(-3i\omega l_A)s_{47}+[\exp(-2i\omega l_A)+\exp(-4i\omega l_A)+\exp(i\omega(l_B'-3l_A))$$
$$+\exp(i\omega(5l_B'-3l_A))]s_{48}+[\exp(i\omega(l_B'-2l_A))+\exp(i\omega(5l_B'-4l_A))]s_{38}$$
$$+[\exp(i\omega(l_B'-4l_A))+\exp(i\omega(5l_B'-2l_A))]s_{58}+[\exp(-i\omega l_A)+\exp(-5i\omega l_A)$$
$$+\exp(i\omega(2l_B'-3l_A))+\exp(i\omega(4l_B'-3l_A))]s_{49}+[1+\exp(i\omega(l_B'-l_A))$$
$$+\exp(2i\omega(l_B'-l_A))+\exp(3i\omega(l_B'-l_A))+\exp(4i\omega(l_B'-l_A))$$
$$+\exp(5i\omega(l_B'-l_A)]s_{28}+\cdots\}, \quad (72)$$

where $s_{47}, s_{48}, \cdots, s_{28}, \cdots$ are the overlap integrals between a $2p\pi$ function located in one ring and a $2p\pi$ function in the other. Thus

$$s_{47}=\int \mathrm{IV}(\nu)\mathrm{VII}(\nu)d\tau_\nu. \quad (73)$$

The overlap integrals $s_{47}, s_{48}, \cdots$ are functions of the internuclear distances between the carbon atoms and may be evaluated in closed form.[15] The value of the integrals decreases rapidly as the distance increases, so that the overlap integrals for $2p\pi$ functions located at extreme ends of the molecule may be neglected. The multiplicity of terms which occur with each s is a result of the fact that the same internuclear distance is associated with more than one pair of atoms. In Table IV the internuclear distances, the equivalent atom pairs, and the overlap integrals are listed. The atoms or $2p\pi$ functions are numbered as shown in Fig. 2 (normal arrangement).

Utilizing the overlap integrals of Table IV we may compute the Δ's. The results are compiled in Table V. Since all of the Δ's are real by direct calculation, it is readily shown that

$$\Delta_{l_A l_B'}=\Delta_{-l_A-l_B'}=\Delta_{l_B' l_A}. \quad (74)$$

In evaluating the normalization and other integrals, a large number of terms of the order of magnitude Δ^2, similar to Eq. (71), and also Δ terms appear. As indicated in Table V, the absolute value of Δ varies little, varying between 0.035 and 0.044. It will therefore be convenient and also greatly simplify the complexities of the computation, without causing appreciable error, if average values for all Δ's and Δ^2's are used. The average value, Δ, is taken as the average of the absolute values of the figures given in Table V with each possible $l_A l_B'$ combination given a weight of one, i.e., $\Delta=0.039$ while $\Delta^2=1.52\times10^{-3}$. From the table it will be observed that all Δ's in which $l_A=\pm1$ are negative in sign. This is a result of the relative phases between the $\phi_{\pm1_A}$ and the $\phi_{l_B'}$ orbitals. Thus $\Delta_{\pm1_A l_B'}$ or $\Delta_{l_B'\pm1_A}$ are to be replaced by $-\Delta$ while all other $\Delta_{l_A l_B'}$'s are to be replaced by $+\Delta$.

Using Eqs. (1A), (2A) and (3A) in Appendix II as outlined in the above, the results given in Table VI below are obtained.

In the derivation of the normalization coefficient, permutations involving powers of Δ greater than Δ^2 were neglected, because of the very small numerical magnitude of such terms.

IX. THE ELECTRONIC INTERACTION ENERGY

In deriving the electronic interaction energy terms it will be instructive to consider in some detail the electronic interaction energy for the ground state of diphenyl, $E_{0D}{}^e$. From Eq. (5A), we need to calculate $h_0(H_D{}^e)$. Using (3A) we can establish the types of integrals involved. Thus, considering terms arising from electrons (1) and (2) we get a benzene Coulomb integral γ_{00} multiplied by Δ^2 which results from an interchange of an electron in ring B with one of the A electrons, numbers 3 to 6. The complete term is $-12\gamma_{00}\Delta^2$ since one interchange changes the

[15] F. Hund, *Handbuch der Physik* (Verlagsbuchhandlung Julius Springer, Berlin, 1933) **24**, No. 1, p. 643.

TABLE IV. Internuclear distances and overlap integrals for diphenyl.

Internuclear distance A		Equivalent distances	Overlap integral
d_{47}[a]	1.48[b]	——	0.225[c]
d_{48}	2.49	d_{37}, d_{57}, $d_{4\,12}$	0.033
d_{38}	2.87	$d_{5\,12}$	0.014
d_{58}	3.75	$d_{3\,12}$	0.002
d_{49}	3.76	$d_{4\,11}$, d_{27}, d_{67}	0.002
d_{28}	4.26	d_{17}, d_{39}, $d_{4\,10}$, $d_{5\,11}$, $d_{6\,12}$	0.0006
$d_{3\,11}$	4.90	$d_{2\,12}$, d_{68}, d_{59}	
d_{18}	5.10	$d_{1\,12}$, $d_{3\,10}$, $d_{5\,10}$	
d_{29}	5.65	$d_{6\,11}$	
$d_{2\,11}$	6.15	d_{69}	
d_{19}	6.46	$d_{1\,11}$, $d_{2\,10}$, $d_{6\,10}$	
$d_{1\,10}$	7.04	——	

[a] d_{47} = distance between atoms 4 and 7.
[b] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940), p. 218.
[c] $s_{47}=0.225$, etc.

sign and since the three α- and β-orbitals in ring B interchanging with the two α- and β-orbitals in ring A, respectively (excluding electrons 1 and 2), make possible 12 different permutations. If we carry out a similar process for the remainder of the electron pairs involved in the integral, we obtain as the total contribution the term $-2E_0{}^e\cdot 12\Delta^2$. This result could readily have been foreseen since each one of the rings taken by itself gives the energy $E_0{}^e$ and the $12P_{AB}$ permutations introduce the factor $-12\Delta^2$. Similar results involving terms like $E_{1S}{}^e$ are obtained for the excited levels. Hence, it will be convenient to list here the value of such terms. Thus:

$$\begin{aligned}
E_0{}^e &= \gamma_{00}+8\gamma_{01}+6\gamma_{11}-4\delta_{01}-2\delta_{1-1} && {}^1\Gamma_1(A_{1g}),\\
E_{1S}{}^e &= E^{(1)e}+\delta_{-12}-\delta_{12}-\xi+2\eta && {}^1\Gamma_9(B_{1u}),\\
E_{2S}{}^e &= E^{(1)e}+\delta_{-12}-\delta_{12}+\xi-2\eta && {}^1\Gamma_{10}(B_{2u}),\\
E_{3S}{}^e &= E^{(1)e}-\delta_{-12}+\delta_{12} && {}^1\Gamma_{12}(E_{1u}),
\end{aligned} \tag{75}$$

where

$$E^{(1)e}=\gamma_{00}+6\gamma_{01}+2\gamma_{02}+3\gamma_{11}+3\gamma_{12}-3\delta_{01}-\delta_{02}-\delta_{1-1}.$$

Equations (75) are obtained from Eqs. (15), (16), and (18) in GMS by deleting the nuclear interaction energy terms ϵ_0, ϵ_1, and ϵ_2 from E_0, $E^{(1)}$, E_{1S}, E_{2S}, E_{3S}.

In the above the integrals $\gamma_{ll'}$ are Coulomb integrals defined by

$$\gamma_{ll'}=\int\int \frac{e^2}{r_{\nu\mu}}|\phi_l(\nu)|^2|\phi_{l'}(\mu)|^2 d\tau_\nu d\tau_\mu, \tag{76}$$

while $\delta_{ll'}$ are exchange integrals, i.e.,

$$\delta_{ll'}=\int\int \frac{e^2}{r_{\nu\mu}}\phi_l(\nu)\phi_{l'}(\mu)[\phi_l(\mu)\phi_{l'}(\nu)]^* d\tau_\nu d\tau_\mu. \tag{77}$$

The terms ξ and η are defined thus:

$$\begin{aligned}
\xi &= \int\int \frac{e^2}{r_{\nu\mu}}\phi_1{}^2(\nu)\phi_2{}^2(\mu)d\tau_\nu d\tau_\mu,\\
\eta &= \int\int \frac{e^2}{r_{\nu\mu}}\phi_1(\nu)\phi_2(\nu)\phi_1(\mu)\phi_2(\mu)d\tau_\nu d\tau_\mu.
\end{aligned} \tag{78}$$

For the diphenyl energy terms we obtain similar Coulomb energy integrals involving one orbital in the A ring and the other in the B ring, i.e.,

$$\gamma_{l_Al_B'}=\int\int \frac{e^2}{r_{\nu\mu}}|\phi_{l_A}(\nu)|^2|\phi_{l_B'}(\mu)|^2 d\tau_\nu d\tau_\mu, \tag{79}$$

also diphenyl exchange integrals,

$$\delta_{l_Al_B'}=\int\int \frac{e^2}{r_{\nu\mu}}\phi_{l_A}(\nu)\phi_{l_B'}(\mu) \times[\phi_{l_A}(\mu)\phi_{l_B'}(\nu)]^* d\tau_\nu d\tau_\mu. \tag{80}$$

Other more complicated diphenyl integrals occur, the general form of which may be represented as

$$[ll',l''l''']=\int\int \frac{e^2}{r_{\nu\mu}}\phi_l{}^*(\nu)\phi_{l'}(\nu) \times\phi_{l''}{}^*(\mu)\phi_{l'''}(\mu)d\tau_\nu d\tau_\mu. \tag{81}$$

The l's in the above may have either subscript A or B.

Returning now to $h_0(H_D{}^e)$, for electrons 1 and 2, we also obtain the terms

$$-2[0_A0_B,\,0_A0_A]\Delta-2[0_A1_B,\,0_A0_A]\Delta -2[0_A-1_B,\,0_A0_A]\Delta, \tag{82}$$

TABLE V. Value of $\Delta_{l_Al_B'}$ for various values of l_A and l_B'.

l_Al_B'	$\Delta_{l_Al_B'}$
0_A0_B	0.041
$0_A\pm1_B$	0.042
$0_A\pm2_B$	0.038
$\pm1_A0_B$	−0.041
1_A1_B, -1_A-1_B	−0.038
1_A-1_B, -1_A1_B	−0.044
1_A2_B, -1_A-2_B	−0.035
1_A-2_B, -1_A2_B	−0.041
$\pm2_A0_B$	0.038
2_A1_B, -2_A-1_B	0.035
2_A-1_B, -2_A1_B	0.041
2_A2_B, -2_A-2_B	0.035
2_A-2_B, -2_A2_B	0.042

TABLE VI. Value of the normalization coefficients N_i, and integrals N_{ij}.

N_i, N_{ij}	Functional equivalent*	Value
N_0		$1-18\Delta_2$
N_1	$4[(a_1N_{11}+a_2N_{11})+(b_1N_{11}+b_2N_{11})]$	$1-16\Delta^2$
N_{-1}	$4[(a_1N_{11}+a_2N_{11})-(b_1N_{11}+b_2N_{11})]$	$1-20\Delta^2$
N_2	$4[(a_1N_{11}-a_2N_{11})+(b_1N_{11}-b_2N_{11})]$	$1-18\Delta^2$
N_{-2}	$4[(a_1N_{11}-a_2N_{11})-(b_1N_{11}-b_2N_{11})]$	$1-18\Delta^2$
N_3	$4[(a_1N_{33}+a_2N_{33})+(b_1N_{33}+b_2N_{33})]$	$1-16\Delta^2$
N_{-3}	$4[(a_1N_{33}+a_2N_{33})-(b_1N_{33}+b_2N_{33})]$	$1-20\Delta^2$
N_4	$4[(a_1N_{33}-a_2N_{33})+(b_1N_{33}-b_2N_{33})]$	$1-18\Delta^2$
N_{-4}	$4[(a_1N_{33}-a_2N_{33})-(b_1N_{33}-b_2N_{33})]$	$1-18\Delta^2$
N_{13}	$4(N_1N_3)^{-\frac{1}{2}}[(a_1N_{13}+a_2N_{13})+(b_1N_{13}+b_2N_{13})]$	$2\Delta^2(1-16\Delta^2)^{-1}$
N_{-1-3}	$4(N_{-1}N_{-3})^{-\frac{1}{2}}[(a_1N_{13}+a_2N_{13})-(b_1N_{13}+b_2N_{13})]$	$-2\Delta^2(1-20\Delta^2)^{-1}$
N_{24}	$4(N_2N_4)^{-\frac{1}{2}}[(a_1N_{13}-a_2N_{13})+(b_1N_{13}-b_2N_{13})]$	$-6\Delta^2(1-18\Delta^2)^{-1}$
N_{-2-4}	$4(N_{-2}N_{-4})^{-\frac{1}{2}}[(a_1N_{13}-a_2N_{13})-(b_1N_{13}-b_2N_{13})]$	$-6\Delta^2(1-18\Delta^2)^{-1}$

*$4a_1N_{11}=4a_1N_{33}=1-18\Delta^2$, $4a_1N_{13}=-3\Delta^2$,
$4a_2N_{11}=4a_2N_{33}=0$, $4a_2N_{13}=3\Delta^2$,
$4b_1N_{11}=4b_1N_{33}=\Delta^2$, $4b_1N_{13}=\Delta^2$,
$4b_2N_{11}=4b_2N_{33}=\Delta^2$, $4b_2N_{13}=\Delta^2$.

which result from interchanging electrons 1 or 2 with 7 or 8, etc. In addition, it is possible to perform another interchange say, in $[0_A0_B, 0_A0_A]$, thus obtaining the term

$$[0_A0_B, 0_A0_B]\Delta^2=\delta_{0_A0_B}\Delta^2.$$

The diphenyl exchange integrals are very small, for example, $\delta_{0_A0_B}=0.018$ ev. Terms containing a diphenyl exchange integral multiplied by Δ^2 are therefore negligible.

The hybrid diphenyl integrals given in (82) are those for which three of the orbitals are in one ring and the fourth is in the second ring. However, one of the two electrons is in two identical orbitals, i.e., 0_A0_A, so that these terms might be called mixed Coulomb integrals. For the electron pair 1 and 3, in addition to getting mixed Coulomb terms such as $[0_A0_A, 1_A0_B]\Delta$ we obtain mixed exchange terms such as $-[0_A0_B, 1_A0_A]\Delta$. The mixed exchange integrals turn out to be considerably smaller than the mixed Coulomb integrals, i.e., the former range in absolute value between 0.05 to 0.10 ev, while the latter vary little in absolute value ranging from 0.26 to 0.30 with an average of 0.27 ev (average for six different integrals). All of the mixed Coulomb terms contribute negative energy terms to $h_0(H_D{}^e)$ while all of the mixed exchange terms are positive contributors. The number of different mixed energy integrals which appear is considerable yet they add little to the value of the energy levels. Hence, in order to simplify the calculation, we replace all of the mixed Coulomb integrals by the average value M, without causing any appreciable error, while we neglect the mixed exchange integrals. It is estimated that the error in the total value of these mixed energy terms caused by neglecting the exchange integrals is less than 10 percent of this total value. Since the latter only affects the location of the final energy levels by possibly 0.2 or 0.3 ev the error caused by dropping the mixed exchange integrals is negligible. In carrying out this simplification it is well to keep in mind that all mixed energy integrals are positive with the exception of those in which one or three of the four orbitals belong to ring A, in which case they are negative.

With these approximations we obtain for $h_0(H_D{}^e)$,

$$h_0(H_D{}^e)=4(\gamma_{0_A0_B}+4\gamma_{0_A1_B}+4\gamma_{1_A1_B})(1-12.5\Delta^2)$$
$$-(2\delta_{0_A0_B}+8\delta_{0_A1_B}+4\delta_{1_A1_B}+4\delta_{1_A-1_B})-360M\Delta-24E_0{}^e\Delta^2. \quad (83)$$

Similarly, for the excited electronic energy terms, ${}_{a_1}h_{ii}{}^e$ (Eq. (1A)) we get

$${}_{4a_1}h_{11}{}^e=(4\gamma_{0_A0_B}+14\gamma_{0_A1_B}+2\gamma_{0_A2_B}+12\gamma_{1_A1_B}+4\gamma_{1_A2_B})(1-12.5\Delta^2)-12(E_0{}^e+E_{1S}{}^e)\Delta^2-12(\xi-2\eta)\Delta^2$$
$$-(2\delta_{0_A0_B}+7\delta_{0_A1_B}+\delta_{0_A2_B}+3\delta_{1_A1_B}+3\delta_{1_A-1_B}+\delta_{1_A2_B}+\delta_{-1_A2_B})-360M\Delta,$$

$$
\begin{aligned}
4a_2h_{11}^e &= 5\{[0_A0_A,\ 2_B-2_B]+2[1_A1_A,\ 2_B-2_B]+[0_A0_A,\ 1_B-1_B] \\
&\qquad +2[1_A1_A,\ 1_B-1_B\}\Delta^2+12(\xi-2\eta)\Delta^2, \\
4b_1h_{11}^e &= 2[-1_A2_A,\ 2_B-1_B](1-12.5\Delta^2)-[-1_A-1_B,\ 2_B2_A] \\
&\qquad -5\{4[1_A-2_A,\ 0_B0_B]+6[1_A-2_A,\ 1_B1_B]\}\Delta^2, \\
4b_2h_{11}^e &= 2[1_A-2_A,\ 2_B-1_B](1-12.5\Delta^2)-[1_A-1_B,\ 2_B-2_A] \\
&\qquad -5\{4[1_A-2_A,\ 0_B0_B]+6[1_A-2_A,\ 1_B1_B]\}\Delta^2, \\
4a_1h_{33}^e &= (4\gamma_{0_A0_B}+14\gamma_{0_A1_B}+2\gamma_{0_A2_B}+12\gamma_{1_A1_B}+4\gamma_{1_A2_B})(1-12.5\Delta^2)-12(E_0^e+E_{3S}^e)\Delta^2 \\
&\qquad -(2\delta_{0_A0_B}+7\delta_{0_A1_B}+\delta_{0_A2_B}+3\delta_{1_A1_B}+3\delta_{1_A-1_B}+\delta_{1_A2_B}+\delta_{-1_A2_B})-360M\Delta, \\
4a_2h_{33}^e &= 5\{[0_A0_A,\ -2_B2_B]+2[1_A1_A,\ 2_B-2_B]+[0_A0_A,\ 1_B-1_B]+2[1_A1_A,\ 1_B-1_B]\}\Delta^2, \\
4b_1h_{33}^e &= 2[1_A2_A,\ 2_B1_B](1-12.5\Delta^2)-[1_A1_B,\ 2_B2_A]-5\{4[1_A2_A,\ 0_B0_B]+6[1_A2_A,\ 1_B1_B]\}\Delta^2, \\
4b_2h_{33}^e &= 2[1_A2_A,\ -2_B-1_B](1-12.5\Delta^2)-[1_A-1_B,\ -2_B2_A]-5\{4[1_A2_A,\ 0_B0_B]+6[1_A2_A,\ 1_B1_B]\}\Delta^2.
\end{aligned}
\tag{84}
$$

In the above, reference to Eqs. (1A) shows that ${}_{a_1}h_{33}^e$ and ${}_{a_2}h_{33}^e$ may be obtained from ${}_{a_1}h_{11}^e$ and ${}_{a_2}h_{11}^e$, respectively, by replacing $l=2_B$ by $l=-2_B$, while ${}_{b_1}h_{33}^e$ and ${}_{b_2}h_{33}^e$ may be obtained from ${}_{b_1}h_{11}^e$ and ${}_{b_2}h_{11}^e$ by replacing $l=-2_A$ by $l=+2_A$ and $l=2_B$ by $l=-2_B$.

In deriving Eqs. (84) use was made of the relationship

$$\gamma_{l_Al_B'}=\gamma_{l_A'l_B},\quad \delta_{l_Al_B'}=\delta_{l_A'l_B}. \tag{85}$$

This may readily be demonstrated by a method analagous to that used in deriving Eq. (32).

We also determine the ${}_{a_k}h_{ij}^e$, from Eqs. (2A). These follow:

$$
\begin{aligned}
4a_1h_{13}^e &= 2([0_A0_A,\ 2_B-2_B]+2[1_A1_A,\ 2_B-2_B])(1-12.5\Delta^2)-[0_A-2_B,\ 2_B0_A]-[1_A-2_B,\ 2_B1_A] \\
&\qquad -[-1_A-2_B,\ 2_B-1_A]-60M\Delta+(-5\gamma_{00}-34\gamma_{01}-21\gamma_{11}+17\delta_{01}+7\delta_{1-1} \\
&\qquad -10\gamma_{0_A0_B}-35\gamma_{0_A1_B}-30\gamma_{1_A1_B})\Delta^2, \\
4a_2h_{13}^e &= -2([0_A0_A,\ 1_B-1_B]+2[1_A1_A,\ 1_B-1_B])(1-12.5\Delta^2)+[0_A-1_B,\ 1_B0_A] \\
&\qquad +[1_A-1_B,\ 1_B1_A]+[1_A-1_B,\ 1_B-1_A]+60M\Delta+(5\gamma_{00}+28\gamma_{01}+15\gamma_{11}+6\gamma_{02}+6\gamma_{12} \\
&\qquad -14\delta_{01}-3\delta_{02}-7\delta_{1-1}+10\gamma_{0_A0_B}+30\gamma_{0_A1_B}+5\gamma_{0_A2_B}+20\gamma_{1_A1_B}+10\gamma_{1_A2_B})\Delta^2, \\
4b_1h_{13}^e &= 2[-1_A-2_A,\ 2_B-1_B](1-12.5\Delta^2)-[-1_A-1_B,\ 2_B-2_A]+10M\Delta \\
&\qquad +5\{3[1_A1_A,\ 2_B-1_B]+2[0_A0_A,\ 2_B-1_B]-3[-1_A-2_A,\ 1_B1_B]-2[-1_A-2_A,\ 0_B0_B]\}\Delta^2, \\
4b_2h_{13}^e &= 2[1_A2_A,\ 2_B-1_B](1-12.5\Delta^2)-[1_A-1_B,\ 2_B2_A]+10M\Delta \\
&\qquad +5\{3[1_A1_A,\ 2_B-1_B]+2[0_A0_A,\ 2_B-1_B]-3[1_A2_A,\ 1_B1_B]-2[1_A2_A,\ 0_B0_B]\}\Delta^2.
\end{aligned}
\tag{86}
$$

${}_{b_2}h_{13}^e$ may be obtained from ${}_{b_1}h_{13}^e$ by replacing $l=-1_A$ by $l=1_A$ and $l=-2_A$ by $l=2_A$.

X. NUCLEAR INTERACTION ENERGY TERMS

The nuclear interaction energy terms ${}_{a_k}h_{ii}^n$ (Eqs. 1A) may be expressed in terms of the following integrals:

$$\epsilon_l=\int[T_{A,B}(\nu)+H_{0A,B}(\nu)]|\phi_{l_{A,B}}(\nu)|^2d\tau_\nu \quad \text{subscript } A \text{ or } B. \tag{87}$$

This is a benzene integral which gives the energy of the lth orbital. In diphenyl, the energy of an electron in the lth orbital of, say, ring A, is affected because it is in the potential field of the "nucleii" of ring B. This results in the integral

$$\lambda_{l_A}=\int|\phi_{l_A}(\nu)|^2H_{0B}{}^A(\nu)d\tau_\nu=\lambda_{l_B}=\int|\phi_{l_B}(\nu)|^2H_{0A}{}^B(\nu)d\tau_\nu. \tag{88}$$

The total energy of an electron in the lth orbital in diphenyl is therefore given by

$$\omega_l=\epsilon_l+\lambda_l. \tag{89}$$

In addition, integrals occur in which an electron is partially in both an A and B orbital. Thus, the energy of an electron partially in both rings due to the nucleii of both rings is given by

$$\omega_{l_Al_B'}=\int\phi_{l_A}^*(\nu)[T_B(\nu)+H_{0B}(\nu)+H_{0A}{}^B(\nu)]\phi_{l_B'}(\nu)d\tau_\nu, \tag{90}$$

where in a manner similar to (89)

$$\omega_{l_Al_B'}=\epsilon_{l_Al_B'}+\lambda_{l_Al_B'},\quad \epsilon_{l_Al_B'}=\int\phi_{l_A}^*(\nu)[T_B(\nu)+H_{0B}(\nu)]\phi_{l_B'}(\nu)d\tau_\nu, \tag{91}$$

$$\lambda_{l_Al_B'}=\int\phi_{l_A}^*(\nu)H_{0A}{}^B(\nu)\phi_{l_B'}(\nu)d\tau_\nu. \tag{92}$$

Also an integral of the form

$$\lambda_{l_Al_A'}=\int\phi_{l_A}^*(\nu)H_{0B}{}^A\phi_{l_A'}(\nu)d\tau_\nu \tag{93}$$

is obtained. This integral evidently represents the potential energy of an electron belonging to two different orbitals of the same ring due to the action of the nucleii in the second ring. In all of the above integrals, the Hamiltonian operators operate on the function which follows the operator.

From symmetry considerations we can reduce the number of integrals which need to be evaluated. The Hamiltonian operators are totally symmetric so that if we perform the rotation $C_2{}^z$ on say (92) we get

$$C_2{}^z\lambda_{l_Al_B'}=\lambda_{l_Al_B'}=\int C_2\phi_{l_B}^*(\nu)H_{0B}{}^A(\nu)C_2\phi_{l_A'}(\nu)d\tau_\nu \text{ or } \lambda_{l_Al_B'}=\lambda_{C_2l_B,C_2l_A'}. \tag{94}$$

A similar symmetry equation holds for both (91) and (93). In the ultimate evaluation of the integrals appearing in the excited state terms, only the real parts need be considered; hence, wherever considered desirable, either the integral or its complex conjugate was used.

The type of interchanges allowed are similar to those obtained in the electronic interaction energy terms, i.e., terms involving both Δ and Δ^2 appear. Thus, for the ground state the nuclear energy is given by

$$N_0E_{0D}{}^n=(4\omega_0+8\omega_1)(1-15\Delta^2)+(-4\omega_{0A}\omega_{0B}-16\omega_{0A}\omega_{1B}+8\omega_{1A}\omega_{1B}+8\omega_{1A}\omega_{-1B})\Delta-48\lambda_{0A}\lambda_{1A}\Delta^2. \tag{95}$$

The term $(4\omega_0+8\omega_1)$ arises from the fact that for the ground state each one of the benzene rings has two electrons in the $l=0$ orbital, two in the $l=1$ orbital, and two in the $l=-1$ orbital. In addition, for any one of the energy terms ω_l which is obtained when electron ν is in orbital l, 15 permutations are possible between the remaining 11 electrons. Thus, suppose ν is in orbital l_A and has the spin α. Then there will remain 2 electrons in ring A having spin α which can be interchanged with 3 electrons in ring B having spin α, thus giving rise to 6 interchanges; also there will remain 3 electrons in ring A having spin β which can be interchanged with three B electrons of spin β, thus causing 9 more interchanges, or a total of 15 interchanges. Each one of the interchanges gives rise to the factor $-\Delta^2$. Since $N_0=1-18\Delta^2$ (Table VI), we may write:

$$(4\omega_0+8\omega_1)(1-15\Delta^2)=(4\omega_0+8\omega_1)N_0+3(4\omega_0+8\omega_1)\Delta^2. \tag{96}$$

For the excited states, the terms are:

$$4_{a_1}h_{11}{}^n=(4\omega_0+7\omega_1+\omega_2)(1-15\Delta^2)+(-4\omega_{0A}\omega_{0B}-14\omega_{0A}\omega_{1B}-2\omega_{0A}\omega_{2B}+6\omega_{1A}\omega_{1B}+6\omega_{1A}\omega_{-1B}$$
$$+2\omega_{1A}\omega_{2B}+2\omega_{-1A}\omega_{2B})\Delta+(-42\lambda_{0A}\lambda_{1A}+6\lambda_{0A}\lambda_{2A}-6\lambda_{1A}\lambda_{-1A}-6\lambda_{1A}\lambda_{2A}+6\lambda_{1A}\lambda_{-2A})\Delta^2,$$
$$4_{a_2}h_{11}{}^n=3(\lambda_{1A}\lambda_{-1A}+2\lambda_{1A}\lambda_{-2A}+\lambda_{2A}\lambda_{-2A})\Delta^2,$$

$$
\begin{aligned}
&4b_1h_{11}{}^n=(\omega 2_A2_B-\omega 1_A1_B)\Delta-10\lambda 1_A{-}2_A\Delta^2,\\
&4b_2h_{11}{}^n=(\omega 2_A{-}2_B-\omega 1_A{-}1_B)\Delta-10\lambda 1_A{-}2_A\Delta^2,\\
&4a_1h_{33}{}^n=(4\omega_0+7\omega_1+\omega_2)(1-15\Delta^2)+(-4\omega 0_A0_B-14\omega 0_A1_B-2\omega 0_A2_B+6\omega 1_A1_B+6\omega 1_A{-}1_B\\
&\qquad\qquad+2\omega 1_A2_B+2\omega{-}1_A2_B)\Delta+(-42\lambda 0_A1_A+6\lambda 0_A2_A-6\lambda 1_A{-}1_A+6\lambda 1_A2_A-6\lambda 1_A{-}2_A)\Delta^2,\\
&4a_2h_{33}{}^n=3(\lambda 1_A{-}1_A+2\lambda 1_A2_A+\lambda 2_A{-}2_A)\Delta^2,\\
&4b_1h_{33}{}^n=(\omega 2_A2_B-\omega 1_A1_B)\Delta-10\lambda 1_A2_A\Delta^2,\\
&4b_2h_{33}{}^n=(\omega 2_A{-}2_B-\omega 1_A{-}1_B)\Delta-10\lambda 1_A2_A\Delta^2.
\end{aligned}
\tag{97}
$$

For the excited states, one of the electrons is in orbital $l=\pm 2$, thus giving rise to the term $4\omega_0+7\omega_1+\omega_2$. From Table VI, we have

$$(4\omega_0+7\omega_1+\omega_2)(1-15\Delta^2)=(4\omega_0+7\omega_1+\omega_2)N_1+(4\omega_0+7\omega_1+\omega_2)\Delta^2. \tag{98}$$

Similarly we may obtain equations for the ${}_{a_k}h_{ij}{}^n$. Thus:

$$
\begin{aligned}
&4a_1h_{13}{}^n=\lambda 2_A{-}2_A(1-15\Delta^2)-2(\omega 0_A2_B-\omega 1_A{-}2_B-\omega 1_A2_B)\Delta-(11\omega_0+19\omega_1-6\lambda 0_A2_A)\Delta^2,\\
&4a_2h_{13}{}^n=-\lambda 1_A{-}1_A(1-15\Delta^2)+2(\omega 0_A1_B-\omega 1_A{-}1_B-\omega 1_A1_B)\Delta\\
&\qquad\qquad+(11\omega_0+16\omega_1+3\omega_2+6\lambda 0_A1_A+3\lambda 1_A2_A+3\lambda 1_A{-}2_A)\Delta^2,\\
&4b_1h_{13}{}^n=(-\omega 1_A1_B+\omega 2_A{-}2_B)\Delta+(2\omega_0+4\omega_1-5\lambda 1_A2_A-5\lambda 1_A{-}2_A)\Delta^2,\\
&4b_2h_{13}{}^n=(-\omega 1_A{-}1_B+\omega 2_A2_B)\Delta+(2\omega_0+4\omega_1-5\lambda 1_A2_A-5\lambda 1_A{-}2_A)\Delta^2.
\end{aligned}
\tag{99}
$$

XI. EVALUATION OF THE ENERGY LEVELS

The numerical values of the energy levels are given by $W_{ij}{}^{\pm}-E_{0D}$ where $W_{ij}{}^{\pm}$ is given by Eq. (24). From the latter it is seen that we need expressions for $\frac{1}{2}(H_{ii}+H_{jj})-E_{0D}$, H_{ii}, H_{ij}, and $(H_{ii}-H_{jj})$.

Using Table VI for the normalization coefficients, Eqs. (53) and (55) for determining the manner in which the individual ${}_{a_k}q_{ii}(\theta)$ are compounded for both the nuclear and electronic terms, and using Eqs. (83), (84), (95), and (97), Table VII may be constructed for the values of H_{ii}, $H_{ii}-H_{jj}$, and $\frac{1}{2}(H_{ii}+H_{jj})-E_0{}^p$. In this table, the following abbreviations are used:

$$
\begin{aligned}
&(88)\qquad \Lambda=4\lambda_0+7\lambda_1+\lambda_2,\quad \Lambda_0=4\lambda_0+8\lambda_1,\quad \Lambda-\Lambda_0=\lambda_2-\lambda_1;\\
&(93)\qquad \Lambda'=-42\lambda 0_A1_A+6\lambda 0_A2_A-6\lambda 1_A{-}1_A;\\
&(89)\qquad \Omega=4\omega_0+7\omega_1+\omega_2,\quad \Omega_0=4\omega_0+8\omega_1,\quad \Omega-\Omega_0=\omega_2-\omega_1;\\
&(91)\qquad \Omega'=-4\omega 0_A0_B-14\omega 0_A1_B-2\omega 0_A2_B+6\omega 1_A1_B+6\omega 1_A{-}1_B+2\omega 1_A2_B+2\omega{-}1_A2_B,\\
&\qquad\quad \Omega_0'=-4\omega 0_A0_B-16\omega 0_A1_B+8\omega 1_A1_B+8\omega 1_A{-}1_B;\\
&(79)\qquad G=4\gamma 0_A0_B+14\gamma 0_A1_B+2\gamma 0_A2_B+12\gamma 1_A1_B+4\gamma 1_A2_B,\\
&\qquad\quad G_0=4\gamma 0_A0_B+16\gamma 0_A1_B+16\gamma 1_A1_B,\\
&\qquad G-G_0=2(\gamma 0_A2_B-\gamma 0_A1_B)+4(\gamma 1_A2_B-\gamma 1_A1_B);\\
&(80)\qquad D=2\delta 0_A0_B+7\delta 0_A1_B+\delta 0_A2_B+3\delta 1_A1_B+3\delta 1_A{-}1_B+\delta 1_A2_B+\delta{-}1_A2_B,\\
&\qquad\quad D_0=2\delta 0_A0_B+8\delta 0_A1_B+4\delta 1_A1_B+4\delta 1_A{-}1_B,\\
&\qquad D-D_0=\delta 0_A2_B-\delta 0_A1_B+\delta 1_A2_B-\delta 1_A1_B+\delta{-}1_A2_B-\delta 1_A{-}1_B.
\end{aligned}
\tag{100}
$$

Numbers in parentheses on the left hand sides of the above equations are references to the equations in the text which define the terms appearing in Eqs. (100).

All of the integrals listed in the table with the exception of some of the bracket integrals such as $[0_B-1_B,\ 1_B0_A]$, $[1_A2_A,\ -2_B1_B]$, and $[1_A2_A,\ 2_B-1_B]$ when evaluated are found to be real. For the complex integrals only the real parts need be taken in accordance with Eq. (55), etc.

Similarly Table VIII may be constructed for the H_{ij} terms from Eqs. (66), (67), (69), (86), and (99).

The numerical value of the various integrals involved may be obtained from the tables given by Sklar and Lyddane[16] for the Coulomb, exchange, and hybrid Coulomb exchange repulsion energies resulting from the repulsion of two $2p\pi$ electrons. In addition the Coulomb and exchange attraction energies of a $2p\pi$ electron for a carbon ion are given. In order to use these tables, a screening constant of $z=3.18$[17] for the carbon atom was used. It was then possible to plot the value of the above integrals as a function of the internuclear distance. Using the distances given in Table IV the various energy integral terms were evaluated. The numerical value of the Coulomb energy integrals given by Sklar and Lyddane extend to internuclear distances of 3.33A only. However, at this value of distance the Coulomb energy has practically become e^2/r, so that this law was used to extrapolate the Coulomb integrals to distances as large as 7A.

In this connection the Coulomb energy terms given in GMS require some revision as a consequence of an error[18] in sign in the original tables of Bartlett[19] from which the Coulomb integrals were determined. The new values as determined from Table 1 of Sklar and Lyddane's paper are:

$$A_1=\int\int \frac{e^2}{r_{\nu\mu}} \mathrm{I}^2(\nu)\,\mathrm{II}^2(\mu)d\tau_\nu d\tau_\mu = 9.05 \text{ volts},$$

$$A_2=\int\int \frac{e^2}{r_{\nu\mu}} \mathrm{I}^2(\nu)\,\mathrm{III}^2(\mu)d\tau_\nu d\tau_\mu = 5.68 \text{ volts},$$

$$A_3=\int\int \frac{e^2}{r_{\nu\mu}} \mathrm{I}^2(\nu)\,\mathrm{IV}^2(\mu)d\tau_\nu d\tau_\mu = 4.98 \text{ volts}.$$

The integrals evaluated by Sklar and Lyddane are the only ones which will occur if interactions between electrons which are not on neighboring atoms are neglected. This assumption was used in the GMS calculation with the exception that Coulomb interaction integrals arising from non-neighbors were retained. In the present work it was found necessary to include the energy terms arising from non-neighbors, since their neglect caused appreciable error. As a consequence expansion of the energy integral terms given in Tables VII and VIII resulted in general integrals of the form

$$(ab;cd)=\int\int a(\nu)b(\nu) \times (e^2/r_{\nu\mu})c(\mu)d(\mu)d\tau_\nu d\tau_\mu, \quad (101)$$

where $a(\nu)$ is the real $2p\pi$ function for electron ν. The integral $(ab;cd)$ was approximated by (reference 3, p. 990)

$$(ab;cd)\simeq s_{ab}s_{cd}\int\int K_{ab}^2(\nu) \times (e^2/r_{\nu\mu})K_{cd}^2(\mu)d\tau_\nu d\tau_\mu, \quad (102)$$

where s_{ab}, s_{cd} are overlap integrals, Eq. (73), and the function $K_{ab}^2(\nu)$ is a $2p\pi$ function located midway between the original a and b functions and similarly for K_{cd}^2. The integral $(ab;cd)$ then becomes equal to a product of two overlap integrals by a Coulomb integral which is evaluated for an internuclear distance corresponding to the distance from the midpoint of a and b to the midpoint of c and d. Similarly, an integral of the form $(ab;cc)$ was approximated by the product of the overlap s_{ab}, with a Coulomb integral between an electron on the $2p\pi$ function c and a $2p\pi$ function located midway between a and b. This same type of approximation was used in evaluating ionic energy terms which had not been tabulated.

Reference to Table VII shows that the center of gravity of the diphenyl levels depends on benzene energy level terms and also on diphenyl terms arising from the interaction between benzene rings. The numerical value (Table IX) of the benzene terms $\frac{1}{2}(E_{1s}+E_{3s})-E_0$ and $\frac{1}{2}(E_{2s}+E_{3s})-E_0$ are obtained from the paper by Goeppert-Mayer and Sklar.

[16] A. L. Sklar and R. H. Lyddane, J. Chem. Phys. **7**, 374 (1939).
[17] C. Zener, Phys. Rev. **36**, 51 (1930).
[18] W. H. Furry and J. H. Bartlett, Jr., Phys. Rev. **44**, 210 (1938), footnote 11, p. 211.
[19] J. H. Bartlett, Jr., Phys. Rev. **37**, 507 (1931).

TABLE VII. Values of H_{ii}, $H_{ii}-H_{jj}$, $\frac{1}{2}(H_{ii}+H_{jj})-E_{0D}$. Numbers in table are

		$[-1_A{}^2{}_A, 2_B-1_B]$	$[1_A-2_A, 2_B-1_B]$	$[1_A{}^2{}_A, 2_B1_B]$	$[1_A{}^2{}_A, -2_B-1_B]$	$[-1_A-1_B, 2_B{}^2{}_A]$	$[1_A-1_B, 2_B-2_A]$	$[1_A1_B, 2_B{}^2{}_A]$	$[1_A-1_B, -2_B{}^2{}_A]$	×Δ 360M	Ω'	Ω_0'	$\omega_{1A}{}_{1B}$	$\omega_{1A}-_{1B}$	$\omega_{2A}{}_{2B}$	$\omega_{2A}-_{2B}$
E_{0D}	$=2E_0+\Lambda_0+G_0-D_0$									−1		1				
H_{11}	$=E_0+E_{1S}+\Lambda+G-D$	2	2			−1	−1			−1	1		−1	−1	1	1
H_{33}	$=E_0+E_{3S}+\Lambda+G-D$			2	2			−1	−1	−1	1		−1	−1	1	1
$H_{11}-H_{33}$	$=E_{1S}-E_{3S}$	2	2	−2	−2	−1	−1	1	1							
$\frac{1}{2}(H_{11}+H_{33})-E_{0D}$	$=\frac{1}{2}(E_{1S}+E_{3S})-E_0+\Lambda-\Lambda_0+G-G_0-(D-D_0)$	1	1	1	1	−½	−½	−½	−½		1	−1	−1	−1	1	1
H_{-1-1}	$=E_0+E_{1S}+\Lambda+G-D$	−2	−2			1	1			−1	1		1	1	−1	−1
H_{-3-3}	$=E_0+E_{3S}+\Lambda+G-D$			−2	−2			1	1	−1	1		1	1	−1	−1
$H_{-1-1}-H_{-3-3}$	$=E_{1S}-E_{3S}$	−2	−2	2	2	1	1	−1	−1							
$\frac{1}{2}(H_{-1-1}+H_{-3-3})-E_{0D}$	$=\frac{1}{2}(E_{1S}+E_{3S})-E_0+\Lambda-\Lambda_0+G-G_0-(D-D_0)$	−1	−1	−1	−1	½	½	½	½		1	−1	1	1	−1	−1
H_{22}	$=E_0+E_{2S}+\Lambda+G-D$	2	−2			−1	1			−1	1		−1	1	1	−1
H_{44}	$=E_0+E_{3S}+\Lambda+G-D$			2	−2			−1	1	−1	1		−1	1	1	−1
$H_{22}-H_{44}$	$=E_{2S}-E_{3S}$	2	−2	−2	2	−1	1	1	−1							
$\frac{1}{2}(H_{22}+H_{44})-E_{0D}$	$=\frac{1}{2}(E_{2S}+E_{3S})-E_0+\Lambda-\Lambda_0+G-G_0-(D-D_0)$	1	−1	1	−1	−½	½	−½	½		1	−1	−1	1	1	−1
H_{-2-2}	$=E_0+E_{2S}+\Lambda+G-D$	−2	2			1	−1			−1	1		1	−1	−1	1
H_{-4-4}	$=E_0+E_{3S}+\Lambda+G-D$			−2	2			1	−1	−1	1		1	−1	−1	1
$H_{-2-2}-H_{-4-4}$	$=E_{2S}-E_{3S}$	−2	2	2	−2	1	−1	−1	1							
$\frac{1}{2}(H_{-2-2}+H_{-4-4})-E_{0D}$	$=\frac{1}{2}(E_{2S}+E_{3S})+\Lambda-\Lambda_0+G-G_0-(D-D_0)$	−1	1	−1	1	½	−½	½	−½		1	−1	1	−1	−1	1

TABLE VIII. Values of H_{ij}. Numbers in table are coefficients

	$\lambda_{1A}-_{1A}$	$\lambda_{2A}-_{2A}$	$[0_A0_A, 1_B-1_B]$	$[0_A0_A, 2_B-2_B]$	$[1_A1_A, 1_B-1_B]$	$[1_A1_A, 2_B-2_B]$	$[-1_A-2_A, 2_B-1_B]$	$[1_A{}^2{}_A, 2_B-1_B]$	$[0_A-1_B, 1_B0_A]$	$[0_A-2_B, 2_B0_A]$	$[1_A-1_B, 1_B1_A]$	$[1_A-1_B, 1_B-1_A]$	$[1_A-1_B, 2_B2_A]$	$[-1_A-1_B, 2_B-2_A]$	$[1_A-2_B, 2_B1_A]$	$[-1_A-2_B, 2_B-1_A]$	×Δ M	$\omega_{0A}{}_{1B}$	$\omega_{0A}{}_{2B}$	$\omega_{1A}-_{1B}$	$\omega_{1A}{}_{1B}$	$\omega_{1A}-_{2B}$	$\omega_{1A}{}_{2B}$	$\omega_{2A}-_{2B}$	$\omega_{2A}{}_{2B}$	ω_0	ω_1	ω_2	$\lambda_{0A}{}_{1A}$	$\lambda_{0A}{}_{2A}$	$\lambda_{1A}-_{1A}$	$\lambda_{1A}-_{2A}$	$\lambda_{1A}{}_{2A}$	$\lambda_{2A}-_{2A}$
$H_{13}=$	−1	1	−2	2	−4	4	2	2	1	−1	1	1	−1	−1	−1	−1	20	2	−2	−3	−3	2	2	1	1	4	5	3	6	6	−1	−7	−7	1
$H_{-1-3}=$	−1	1	−2	2	−4	4	−2	−2	1	−1	1	1	1	1	−1	−1	−20	2	−2	−1	−1	2	2	−1	−1	−4	−11	3	6	6	−5	13	13	5
$H_{24}=$	1	1	2	2	4	4	2	−2	−1	−1	−1	−1	−1	−1	−1	−1	−120	−2	−2	3	1	2	2	1	−1	−22	−35	−3	−6	6	3	−3	−3	3
$H_{-2-4}=$	1	1	2	2	4	4	−2	2	−1	−1	−1	−1	1	1	−1	−1	−120	−2	−2	1	3	2	2	−1	1	−22	−35	−3	−6	6	3	−3	−3	3

In the course of this investigation the benzene energy levels were recomputed including all energy terms arising from non-neighbors. It was found that the levels computed in GMS were too low by approximately 3 ev as given in Table X.

Goeppert-Mayer, in a private communication has indicated that similar results were obtained in a recalculation of the benzene levels including the effect of neighbors and neighbors once-removed. The new calculations are in poorer agreement with experiment in benzene and if used to determine the center of gravity of the diphenyl levels will cause poor agreement with experiment. Consequently we use the original values of 8.0, 5.8 and 5.0 for ${}^1\Gamma_{12}$, ${}^1\Gamma_9$, ${}^1\Gamma_{10}$ in the diphenyl calculation as the best estimate of the experimental values for the benzene energy levels.

The term $\Lambda-\Lambda_0+G-G_0+D-D_0$ is common to all energy levels.

coefficients of terms appearing at top—Multiply by Δ or Δ^2, as indicated.

| | | |

TABLE IX. Numerical values of various integrals and energy level terms.

$\frac{1}{2}(E_{1s}+E_{3s})-E_0$	6.9 volts	$\Omega\Delta^2$	−1.30 volts
$\frac{1}{2}(E_{2s}+E_{3s})-E_0$	6.5	$\Omega_0\Delta^2$	−1.32
γ_{0A0B}	3.49	$E_0^e\Delta^2$	0.180
γ_{0A1B}	3.51	$E_{1s}^e\Delta^2$	0.181
γ_{0A2B}	3.54	$E_{2s}^e\Delta^2$	0.179
γ_{1A1B}	3.49	$E_{3s}^e\Delta^2$	0.186
γ_{1A2B}	3.52	$G\Delta^2$	0.192
$\lambda_2-\lambda_1$	−0.09	$G_0\Delta^2$	0.191
$\Lambda-\Lambda_0+G-G_0$	+0.09	$\Lambda'\Delta^2$	−0.234
δ_{0A0B}	0.022	$[0_A0_A,\ 1_B-1_B]$	0.124
δ_{0A1B}	0.023	$[0_A0_A,\ 2_B-2_B]$	0.148
δ_{0A2B}	0.018	$[1_A1_A,\ 2_B-2_B]$	0.179
δ_{1A1B}	0.021	$Re[1_A1_A,\ -2_B1_B]$	−0.059
$[-1_A2_A,\ 2_B-1_B]$	−0.045	$Re[1_A2_A,\ 2_B-1_B]$	−0.044
$[1_A-2_A,\ 2_B-1_B]$	−0.044	M	0.27
$[1_A2_A,\ 2_B1_B]$	−0.090	$\omega_0\Delta^2$	−0.112
$[1_A2_A,\ -2_B-1_B]$	−0.359	$\omega_1\Delta^2$	−0.109
$\Omega'-\Omega_0'$	−1.20	$\omega_2\Delta^2$	−0.0947
ω_{0A0B}	−3.47	γ_{00}	9.11
ω_{0A1B}	−3.57	γ_{01}	9.02
ω_{0A2B}	−3.38	γ_{02}	8.78
ω_{1A1B}	3.44	γ_{11}	8.95
ω_{1A-1B}	3.86	γ_{12}	8.43
ω_{1A2B}	3.18	δ_{01}	3.12
ω_{-1A2B}	3.71	δ_{02}	1.67
ω_{2A2B}	−3.00	δ_{1-1}	1.97
ω_{2A-2B}	−3.68		
λ_{0A1A}	3.67	σ_0	1.616
λ_{0A2A}	−1.13	σ_1	1.203
λ_{1A-1A}	−1.18	σ_2	0.719
λ_{1A-2A}	0.65	Δ	0.039
λ_{1A2A}	3.75	Δ^2	0.00152
λ_{2A-2A}	−0.99	N_{13}	0.00311
		N_{-1-3}	−0.00295
		$N_{24}=N_{-2-4}$	−0.00937

with a similar expression holding for $|\phi_{l_B'}|^2$, we get

$$36\sigma_{l_A}\sigma_{l_B'}\gamma_{l_Al_B'}=\int\int\left\{\left[S_A^2(\nu)+2\cos\left(\frac{2\pi l_A}{6}\right)S_{12A}(\nu)+2\cos\left(\frac{4\pi l_A}{6}\right)S_{13A}(\nu)+(-1)^{l_A}S_{14A}(\nu)\right]e^2/r_{\nu\mu}\right.$$

$$\left.\times\left[S_B^2(\mu)+2\cos\left(\frac{2\pi l_B'}{6}\right)S_{12B}(\mu)+2\cos\left(\frac{4\pi l_B'}{6}\right)S_{13B}(\mu)+(-1)^{l_B'}S_{14B}(\mu)\right]\right\}d\tau_\nu d\tau_\mu, \quad (104)$$

where

$$S_A^2=\sum_{K_i=\mathrm{I}}^{\mathrm{VI}}K_i^2; \qquad S_B^2=\sum_{K_i=\mathrm{VII}}^{\mathrm{XII}}K_i^2$$

$$S_{12A}=\sum_{K_i=\mathrm{I}}^{\mathrm{VI}}K_iK_{i+1}; \quad S_{12B}=\sum_{K_i=\mathrm{VII}}^{\mathrm{XII}}K_iK_{i+1}$$

$$S_{13A}=\sum_{K_i=\mathrm{I}}^{\mathrm{VI}}K_iK_{i+2}; \quad S_{13B}=\sum_{K_i=\mathrm{VII}}^{\mathrm{XII}}K_iK_{i+2} \quad (105)$$

$$S_{14A}=\sum_{K_i=\mathrm{I}}^{\mathrm{VI}}K_iK_{i+3}; \quad S_{14B}=\sum_{K_i=\mathrm{VII}}^{\mathrm{XII}}K_{i+3}$$

in which

$$K_{6+1}=K_{5+2}=K_{4+3}=\mathrm{I}, \quad K_{6+2}=K_{5+3}=\mathrm{II}, \quad K_{6+3}=\mathrm{III}$$

and

$$K_{12+1}=K_{11+2}=K_{10+3}=\mathrm{VII}, \quad K_{12+2}=K_{11+3}=\mathrm{VIII}, \quad K_{12+3}=\mathrm{IX}.$$

The integral (104) can be separated into a number of terms, a typical one of which is

$$\int\int \mathrm{I}^2(\nu)e^2/r_{\nu\mu}\left[\mathrm{VII}^2(\mu)+2\cos\left(\frac{2\pi l_B'}{6}\right)\mathrm{VII}(\mu)\mathrm{VIII}(\mu)\right.$$
$$\left.+2\cos\left(\frac{4\pi l_B'}{6}\right)\mathrm{VII}(\mu)\mathrm{IX}(\mu)+(-1)^{l_B'}\mathrm{VII}(\mu)\mathrm{X}(\mu)\right]d\tau_\nu d\tau_\mu. \quad (106)$$

In accordance with our previous discussion an integral such as

$$\int\int \mathrm{I}^2(\nu)e^2/r_{\nu\mu}\mathrm{VII}(\mu)\mathrm{VIII}(\mu)d\tau_\nu d\tau_\mu$$

is replaced by

$$s_{78}\int\int \mathrm{I}^2(\nu)e^2/r_{\nu\mu}K_{78}^2(\mu)d\tau_\nu d\tau_\mu, \text{ etc.}$$

However, if (VII, VIII) were replaced by VII^2 instead of K_{78}^2, (VII, IX) by VII^2, etc. (106) would become

$$\left[1+2s_1\cos\left(\frac{2\pi l_B'}{6}\right)+2s_2\cos\left(\frac{4\pi l_B'}{6}\right)+(-1)^{l_B'}s_3\right]\int\int \mathrm{I}^2(\nu)\frac{e^2}{r_{\nu\mu}}\mathrm{VII}^2(\mu)d\tau_\nu d\tau_\mu, \quad (107)$$

where s_1 is the overlap integral between neighbors in the benzene ring, s_2 between neighbors once-removed and s_3 between neighbors twice-removed. The expression in brackets in (107) is exactly $\sigma_{l_B'}$ (Eq. (19) GMS). In addition to the term (106) there are similar terms in which $\mathrm{I}^2(\nu)$ is replaced by

$$2\cos\left(\frac{2\pi l_A}{6}\right)\mathrm{I}(\nu)\mathrm{II}(\nu), \quad 2\cos\left(\frac{4\pi l_A}{6}\right)\mathrm{I}(\nu)\mathrm{III}(\nu), \quad (108)$$

and $(-1)^{l_A}\mathrm{I}(\nu)\mathrm{IV}(\nu)$ successively. These terms combined with (107) result in the term

$$\sigma_{l_A}\sigma_{l_B'}\int\int \mathrm{I}^2(\nu)e^2/r_{\nu\mu}\mathrm{VII}^2(\mu)d\tau_\nu d\tau_\mu. \quad (109)$$

Evidently, under these assumptions (104) may be written as (see 105)

$$36\sigma_{l_A}\sigma_{l_B'}\gamma_{l_Al_B'}=\sigma_{l_A}\sigma_{l_B'}\int\int S_A^2(\nu)\frac{e^2}{r_{\nu\mu}}S_B^2(\mu)d\tau_\nu d\tau_\mu, \quad (110)$$

so that

$$\gamma_{l_Al_B'}\simeq\frac{1}{36}\int\int S_A^2(\nu)\frac{e^2}{r_{\nu\mu}}S_B^2(\mu)d\tau_\nu d\tau_\mu=3.52 \text{ volts}. \quad (111)$$

Comparison of (111) with the values given in Table IX, which were obtained by using the fictitious centrally-located $2p\pi$ function approximation, shows the extent of agreement between the two types of approximations.

The diphenyl exchange integrals $\delta_{l_Al_B'}$ are all very small, approximately 0.02 volt. This results from the fact that the double exchange between rings gives rise to integrals whose numerical values are proportional to the product of two overlap integrals (Table V). As a consequence, $D-D_0$ is completely negligible.

The λ_l integrals (Eq. (88)) are practically independent of the value of l. As in the benzene case, we set the potential term

$$H_{0B}{}^A(\nu)=\sum_{K_B}\mathbf{H}_{K_B}(\nu)-\int S_B^2(\mu)e^2/r_{\nu\mu}=\sum_{K_B}H_{K_B}, \quad (112)$$

i.e., the potential acting on an electron in ring A as a result of the carbon ions in ring B is the sum-

mation of the potential H_{K_B} due to each individual carbon ion and the same as that due to the neutral carbons atoms in ring B, $\sum_{K_B} \mathbf{H}_{K_B}(\nu)$, minus the potential caused by the $2p\pi$ electrons in ring B. From (88), (103), and (105) we have

$$\lambda_l=\frac{1}{6\sigma_l}\int\left[S_A^2(\nu)+2\cos\left(\frac{2\pi l_A}{6}\right)S_{12_A}(\nu)+2\cos\left(\frac{4\pi l_A}{6}\right)S_{13_A}(\nu)+(-1)^{l_A}S_{14_A}(\nu)\right]\sum_{K_B}\mathbf{H}_{K_B}(\nu)d\tau_\nu$$

$$-\frac{1}{6\sigma_l}\int\int\left[S_A^2(\nu)+2\cos\left(\frac{2\pi l_A}{6}\right)S_{12_A}(\nu)+2\cos\left(\frac{4\pi l_A}{6}\right)S_{13_A}(\nu)\right.$$

$$\left.+(-1)^{l_A}S_{14_A}(\nu)\right]\frac{e^2}{r_{\nu\mu}}S_B^2(\mu)d\tau_\nu d\tau_\mu. \quad (113)$$

For reasons similar to those used in obtaining the approximate value of $\gamma_{l_A l_B'}$, (113) becomes approximately

$$\lambda_l\simeq\frac{1}{6}\int S_A^2(\nu)\sum_{K_B}\mathbf{H}_{K_B}(\nu)d\tau_\nu-\frac{1}{6}\int\int S_A^2(\nu)\frac{e^2}{r_{\nu\mu}}S_B^2(\mu)d\tau_\nu d\tau_\mu=-21.23 \text{ volts}. \quad (114)$$

Note that in Table IX, $\lambda_2-\lambda_1$ was calculated directly by an appropriate grouping of differences of small terms.

The location of the energy levels also depends on the square bracket terms such as $[-1_A 2_A, 2_B-1_B]$ which are relatively small in magnitude. The bracket terms such as $[-1_A-1_B, 2_B 2_A]$ are really exchange integrals since each electron is partially in ring A and in ring B. Their approximate value is 0.02 volts; hence, in combination with the factor of $\frac{1}{2}$ they may be neglected.

The terms which contain Δ as a factor are all of the form $\omega_{l_A l_B'}$ (Eq. (90)). These are computed in the following manner: From (92) and (112) we have

$$\lambda_{l_A l_B'}=\int\phi_{l_A}^*(\nu)\phi_{l_B'}(\nu)\left[\sum_{K_A}\mathbf{H}_{K_A}(\nu)\right]d\tau_\nu-\int\int\phi_{l_A}^*(\nu)\phi_{l_B'}(\nu)\frac{e^2}{r_{\nu\mu}}S_A^2(\mu)d\tau_\nu d\tau_\mu, \quad (115)$$

also from (91) and (3)

$$\epsilon_{l_A l_B'}=\frac{1}{(6\sigma_{l'})^{\frac{1}{2}}}\int\phi_{l_A}^*(\nu)\left[T_B(\nu)+\sum_{K_B}H_{K_B}(\nu)\right][\mathrm{VII}(\nu)+e^{i\omega l'}\mathrm{VIII}(\nu)+\cdots+e^{5i\omega l'}\mathrm{XII}(\nu)]d\tau_\nu. \quad (116)$$

Equation (116) may also be written as

$$\epsilon_{l_A l_B'}=\frac{1}{(6\sigma_{l'})^{\frac{1}{2}}}\int\phi_{l_A}^*(\nu)\{[T_B(\nu)+H_{\mathrm{VII}}(\nu)]\mathrm{VII}(\nu)+[T_B(\nu)+H_{\mathrm{VIII}}(\nu)]e^{i\omega l'}\mathrm{VIII}(\nu)+\cdots$$

$$+[T_B(\nu)+H_{\mathrm{XII}}(\nu)]e^{5i\omega l'}\mathrm{XII}(\nu)\}d\tau_\nu+\int\phi_{l_A}^*(\nu)\sum_{K_B}H_{K_B}(\nu)\phi_{l_B'}(\nu)d\tau_\nu$$

$$-\frac{1}{(6\sigma_{l'})^{\frac{1}{2}}}\int\phi_{l_A}^*(\nu)\{H_{\mathrm{VII}}(\nu)\mathrm{VII}(\nu)+\cdots+H_{\mathrm{XII}}e^{5i\omega l'}\mathrm{XII}(\nu)\}d\tau_\nu. \quad (117)$$

Since $\mathrm{VII}(\nu)$, $\mathrm{VIII}(\nu)$, $\cdots$ are atomic wave functions we may write (GMS)

$$[T(\nu)+H_{\mathrm{VII}}(\nu)]\mathrm{VII}(\nu)=W_{2p}\mathrm{VII}(\nu), \quad (118)$$

etc., where W_{2p} is the energy of a $2p$ electron, in the unexcited carbon atom. Thus, the first integral of (117) becomes equal to $\Delta_{l_A l_B'}W_{2p}$. Expanding $\sum_{K_B}H_{K_B}$ in the second integral of (117) and adding

the resulting value of $\epsilon_{l_A l_B'}$ to $\lambda_{l_A l_B'}$, we obtain the final result

$$\omega_{l_A l_B'} = \Delta_{l_A l_B'} W_{2P} + \int \phi_{l_A}^*(\nu)\phi_{l_B'}(\nu)\left[\sum_{K=I}^{K=XII} \mathbf{H}_K(\nu)\right]d\tau_\nu$$

$$-\int\int \phi_{l_A}^*(\nu)\phi_{l_B'}(\nu)\frac{e^2}{r_{\nu\mu}}\left[\sum_{K=I}^{K=XII} K^2(\mu)\right]d\tau_\nu d\tau_\mu - \int \phi_{l_A}^*(\nu)[\textstyle\sum' H_{K_B}(\nu)]\phi_{l_B'}(\nu)d\tau_\nu, \quad (119)$$

where $\sum'$ is a summation in which all terms are zero other than those for which K_B in $\phi_{l_B'}$ has the same value as K_B in H_{K_B}, as in the third integral of (117).

For the value of W_{2p}, the experimental value[20] of -11.24 volts obtained from ionization potential data was used. Since W_{2p} occurs with the factor $\Delta_{l_A l_B'}$, the value of $\omega_{l_A l_B'}$ is not strongly dependent on W_{2p}.

The evaluation of terms containing Δ^2 as a factor involves the determination of the value of integrals not previously considered such as $\lambda_{l_A l_A'}$ (Eq. (93)). An expansion similar in nature to (115) for $\lambda_{l_A l_B'}$ holds for these integrals.

Other Δ^2 terms which occur such as Ω, Ω_0, E_0^e, E_{1s}^e, E_{2s}^e, E_{3s}^e have rather large numerical values since they depend on the energy of the orbitals, i.e., ω_l (Eq. (89)), or on benzene integrals (Eq. (75)). However, in combination with the factor Δ^2, their contribution is moderate.

The effect of the bracket integrals, such as $[0_A 0_A,\ 1_B - 1_B]$ when multiplied by the factor Δ^2 is completely negligible.

Terms in H_{ij} such as $\omega_0\Delta^2$, $\omega_1\Delta^2$, and $\omega_2\Delta^2$ strongly influence the value of H_{ij} because of their relatively large values and the large coefficients with which they appear. However, their contribution to the value of H_{ij} is generally partially compensated for by the benzene γ and δ integrals and by diphenyl γ integrals.

Reference to Eq. (24) shows that the energy levels also depend on the value of N_{ij}. From Table IX, evidently $N_{ij}^2 \ll 1$, so that in expressing $W_{ij}^{\pm} - E_{0D}$ as given in Table VII, the coefficient $1/(1-N_{ij}^2)$ is simply taken as 1.

TABLE X. Benzene energy levels—ev.

		GMS	London
$E_{3s}-E_0$	$^1\Gamma_{12}$	8.0	11.1
$E_{1s}-E_0$	$^1\Gamma_9$	5.8	8.8
$E_{2s}-E_0$	$^1\Gamma_{10}$	5.0	7.3
$E_{2t}-E_0$	$^3\Gamma_{10}$	3.0	7.2
$E_{3t}-E_0$	$^3\Gamma_{12}$	2.2	5.8
$E_{1t}-E_0$	$^3\Gamma_9$	1.5	4.5

[20] A. E. Ruark and H. C. Urey, *Atoms, Molecules, and Quanta* (McGraw-Hill Book Company, Inc., New York, 1930), p. 280.

Using the numerical values listed in Table IX, and Eq. (24), the energy levels depicted in Fig. 4 are obtained. From considerations following Eq. (24) it is clear that if both H_{ij} and N_{ij} were zero, the energy levels would simply be W_{ii} and W_{jj}. Thus the 5-volt level in benzene would result in levels W_{22} and W_{-2-2}. However, because of the interaction between Φ_2^D and Φ_4^D, the value of W_{22} shifts slightly to W_{24}^-, while W_{-2-2} becomes W_{-2-4}^-. Thus the 5-volt level in benzene has been split into the two levels, 4.9 volts and 5.2 volts. It will be recalled that the 5-volt level in benzene gave a forbidden transition to the ground state. In diphenyl, however, the 5.2-volt level gives an allowed electronic transition, so that the weak 5.0-volt transition in benzene gives rise to a strong transition in diphenyl.

Similarly, the forbidden 5.8-volt transition in benzene gives rise to an allowed 6.6-volt and forbidden 5.4-volt transition. The 8.0-volt $^1\Gamma_{12}$

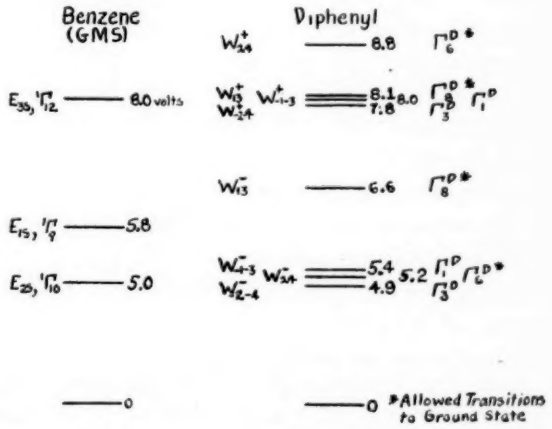

FIG. 4. Benzene and diphenyl energy levels.

level which gives an allowed transition in benzene gives rise to four levels two of which have allowed transitions.

Experimentally, the ultraviolet absorption spectrum of diphenyl in the vapor phase[21] shows a minimum absorption at 5.9 volts and also at 6.9 volts with a maximum in the absorption band at about 6.4 volts. Also a broad maximum occurs from about 7.3 volts to 7.6 volts which was the shortest wave-length used in these experiments. The ultraviolet absorption spectrum of diphenyl in the vapor state has been investigated by Beck[22] at the Catholic University of America. These measurements show the existence of a very broad absorption band from about 2200A to 2800A, i.e., from about 5.6 to 4.4 volts. Thus, the levels shown in Fig. 4 are in good agreement with the experimental observations.

In Carr and Stücklen's paper the absorption bands are very broad and show very little vibration structure. The band observed by Beck is completely diffuse and shows no vibration structure. It is believed that the diffuseness in the observed bands may be partly due to the overlapping of the several electronic levels involved.

XIII. SUMMARY AND CONCLUSIONS

The diphenyl wave functions are set up as linear combinations of molecular benzene functions, and in such a way as to have the same symmetry as diphenyl. These wave functions are next antisymmetrized with respect to the interchange of any two electrons by including the appropriate spin factor in the functions. As a consequence of this procedure the secular determinant automatically factors into four quadratic equations from which the diphenyl energy levels may be determined. The center of gravity of the diphenyl (singlet) levels is shown to depend on the benzene singlet levels previously computed by Goeppert-Mayer and Sklar. In the calculation of the position of the levels, a large number of integrals occur as a consequence of the interaction between the two benzene rings of diphenyl. All integrals are considered in the evaluation of the energy levels up to terms containing Δ^2, the square of the overlap integral, as a factor. The integrals which must be evaluated are of two types, electronic, involving the interaction between two $2p\pi$ electrons, and ionic or nuclear involving the interaction between a $2p\pi$ electron and a carbon ion or $2p\pi$-less carbon atom. The numerical value of integrals of the required type for the case where only interactions between neighbors are considered, with the exception of Coulomb integrals, are available in the literature. In this paper the restriction that the calculation be confined to neighbors, was dropped. The effect of all non-neighbors was determined by suitable approximation formulae. The resulting energy levels are in fairly good agreement with the experimental observations.

All of the numerical values of the energy integrals are based on internuclear distances computed on the basis of a flat plane structure for diphenyl. The good agreement between theory and experiment therefore supports the hypothesis of the coplanarity of the two benzene rings.

The method carried out in this paper for progressing from a known solution for a relatively simple molecule, such as benzene, to the problem of obtaining a solution for a more complicated molecule, such as diphenyl, is believed illustrative of the procedure which may be carried out in similar cases or in building up to more complicated molecules. Furthermore, it has also been demonstrated here that the method of antisymmetric orbitals is suitable for use in determining the splitting of known energy levels which may be caused by the presence of a perturbing influence or interaction of some kind.

In carrying out the calculations of the energy levels, it was found necessary to consider the electronic and nuclear interactions separately. A method which would appear to have inherently greater accuracy would be to consider the electronic and nuclear interactions jointly. In this case, the energy integrals which occur are essentially due to the interaction between a $2p\pi$ electron and a neutral atom. Since these integrals have small numerical values, the levels would be obtained as a summation of small terms. In the present method the levels are partially dependent on differences between electronic and nuclear integrals which are larger in magnitude than the

[21] E. Carr and J. Stücklen, J. Chem. Phys. **4**, 760 (1936).
[22] Private communication.

electronic-neutral atom interaction. However, it was found difficult to carry out the proposed method, since a one-to-one matching between electronic and nuclear terms was not possible in all cases, and since the values of the resulting penetration integrals had not previously been evaluated, with the exception of neighbor interactions.

The author is indebted to Professors K. F. Herzfeld and A. L. Sklar for many helpful discussions and much assistance and guidance in connection with this work.

APPENDIX I

In order to bring out the meaning of the permutation operator P_{AB} given in Eq. (37) we carry out the details of the proof sketched in the above for Eq. (50).

Consider the one-electron orbitals which make up the integrand of ${}_{b_1}h_{11}{}^{e}$ [see ${}_{b_1}q_{11}(\theta)$ in Eq. (1A) in Appendix II]. We do not write the orbitals for electrons (1), (2), (7), and (8) since they will remain unchanged in future operations. Thus, writing the terms of the integrand only, we have

$$\text{in } {}_{b_1}h_{11}{}^{e}\text{: } [\overset{\alpha}{\phi}_{1A}(3)\overset{\beta}{\phi}_{1A}(4)\overset{\alpha}{\phi}_{-1A}(5)\overset{\beta}{\phi}_{-1A}(6)\overset{\alpha}{\phi}_{1B}(9)\overset{\beta}{\phi}_{1B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1B}(11)\phi_{2B}(12)]^{*}H_{D}{}^{e}$$

$$\times P_{AB}[\overset{\alpha}{\phi}_{1A}(3)\overset{\beta}{\phi}_{1A}(4)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1A}(5)\phi_{2A}(6)\overset{\alpha}{\phi}_{1B}(9)\overset{\beta}{\phi}_{1B}(10)\overset{\alpha}{\phi}_{-1B}(11)\overset{\beta}{\phi}_{-1B}(12)], \quad (1')$$

and

$$\text{in } ({}_{b_1}h_{11}{}^{e})^{*}\text{: } [\overset{\alpha}{\phi}_{-1A}(3)\overset{\beta}{\phi}_{-1A}(4)\overset{\alpha}{\phi}_{1A}(5)\overset{\beta}{\phi}_{1A}(6)\overset{\alpha}{\phi}_{-1B}(9)\overset{\beta}{\phi}_{-1B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1B}(11)\phi_{-2B}(12)]^{*}H_{D}{}^{e}$$

$$\times P_{AB}[\overset{\alpha}{\phi}_{-1A}(3)\overset{\beta}{\phi}_{-1A}(4)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1A}(5)\phi_{-2A}(6)\overset{\alpha}{\phi}_{-1B}(9)\overset{\beta}{\phi}_{-1B}(10)\overset{\alpha}{\phi}_{1B}(11)\overset{\beta}{\phi}_{1B}(12)], \quad (2')$$

which is obtained by taking the complex conjugate of everything inside the square brackets.

Now let us change the name of the integration variables throughout the entire integrand in the following manner: 3↔5, 4↔6, and (2′) becomes

$$[\overset{\alpha}{\phi}_{1A}(3)\overset{\beta}{\phi}_{1A}(4)\overset{\alpha}{\phi}_{-1A}(5)\overset{\beta}{\phi}_{-1A}(6)\overset{\alpha}{\phi}_{-1B}(9)\overset{\beta}{\phi}_{-1B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1B}(11)\phi_{-2B}(12)]^{*}H_{D}{}^{e}$$

$$\times P_{AB}[\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1A}(3)\phi_{-2A}(4)\overset{\alpha}{\phi}_{-1A}(5)\overset{\beta}{\phi}_{-1A}(6)\overset{\alpha}{\phi}_{-1B}(9)\overset{\beta}{\phi}_{-1B}(10)\overset{\alpha}{\phi}_{1B}(11)\overset{\beta}{\phi}_{1B}(12)]. \quad (3')$$

The integrand for ${}_{b_4}h_{11}{}^{e}$ is

$$[\overset{\alpha}{\phi}_{1A}(3)\overset{\beta}{\phi}_{1A}(4)\overset{\alpha}{\phi}_{-1A}(5)\overset{\beta}{\phi}_{-1A}(6)\overset{\alpha}{\phi}_{-1B}(9)\overset{\beta}{\phi}_{-1B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1B}(11)\phi_{-2B}(12)]^{*}H_{D}{}^{e}$$

$$\times P_{AB}[\overset{\alpha}{\phi}_{-1A}(3)\overset{\beta}{\phi}_{-1A}(4)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1A}(5)\phi_{-2A}(6)\overset{\alpha}{\phi}_{1B}(9)\overset{\beta}{\phi}_{1B}(10)\overset{\alpha}{\phi}_{-1B}(11)\overset{\beta}{\phi}_{-1B}(12)]. \quad (4')$$

Terms in ${}_{b_4}h_{11}{}^{e}$ will be different from zero only if they contain no more than two unmatched orbitals. In accordance with the definition of P_{AB}, in Eq. (4′) we perform the matching permutations 3↔5, 4↔6, 9↔11, 10↔12, thus leaving the unmatched pair

$$[\phi_{1A}(4)\phi_{-2B}(12)]^{*}H_{D}{}^{e}[\phi_{-2A}(4)\phi_{1B}(12)]. \quad (5')$$

Evidently the above permutation transforms Eq. (4′) into (3′) thus showing that

$$({}_{b_1}h_{11}{}^{e})^{*} = {}_{b_4}h_{11}{}^{e}.$$

The unmatched pair (5′) represents an identity permutation in the class P_{AB} since it involves one electron in ring A and one in ring B. Furthermore it gives rise to an integral which results from the interaction between an electron in ring A and one in ring B. Consequently, it will be seen that the class of P_{AB} permutations leads to integrals which represent the interaction between rings.

APPENDIX II

Value of the integrals ${}_{a_k}q_{ii}(\theta)$ in terms of the one-electron orbitals

$$
\begin{aligned}
{}_{a_1}q_{11}(\theta) = \frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[&\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{2_B}(12)]^*\theta\\
&\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{2_B}(12)]\}d\tau,
\end{aligned}
$$

$$
\begin{aligned}
{}_{a_2}q_{11}(\theta) = \frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[&\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{2_B}(12)]^*\theta\\
&\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{-1_B}(9)\overset{\beta}{\phi}_{-1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1_B}(11)\phi_{-2_B}(12)]\}d\tau,
\end{aligned}
$$

$$
\begin{aligned}
{}_{b_1}q_{11}(\theta) = \frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[&\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{2_B}(12)]^*\theta\\
&\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_A}(5)\phi_{2_A}(6)\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{\alpha}{\phi}_{-1_B}(11)\overset{\beta}{\phi}_{-1_B}(12)]\}d\tau,
\end{aligned}
$$

$$
\begin{aligned}
{}_{b_2}q_{11}(\theta) = \frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[&\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{1_A}(5)\overset{\beta}{\phi}_{-1_A}\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{2_B}(12)]^*\theta\\
&\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{-1_A}(3)\overset{\beta}{\phi}_{-1_A}(4)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1_A}(5)\phi_{-2_A}(6)\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{\alpha}{\phi}_{-1_B}(11)\overset{\beta}{\phi}_{-1_B}(12)]\}d\tau,
\end{aligned}
$$

$$
\begin{aligned}
{}_{a_1}q_{33}(\theta) = \frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[&\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{-2_B}(12)]^*\theta\\
&\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)\\
&\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{-2_B}(12)]\}d\tau, \quad (1A)
\end{aligned}
$$

$$
{}_{a_2}q_{33}(\theta)=\frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{-2_B}(12)]^*\theta
$$

$$
\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{-1_B}(9)\overset{\beta}{\phi}_{-1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1_B}(11)\phi_{2_B}(12)]\}d\tau,
$$

$$
{}_{b_1}q_{33}(\theta)=\frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{-2_B}(12)]^*\theta
$$

$$
\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_A}(5)\phi_{-2_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{\alpha}{\phi}_{-1_B}(11)\overset{\beta}{\phi}_{-1_B}(12)]\}d\tau,
$$

$$
{}_{b_2}q_{33}(\theta)=\frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{-2_B}(12)]^*\theta
$$

$$
\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{-1_A}(3)\overset{\beta}{\phi}_{-1_A}(4)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1_A}(5)\phi_{2_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{\alpha}{\phi}_{-1_B}(11)\overset{\beta}{\phi}_{-1_B}(12)]\}d\tau.
$$

In the above set of integrals, for $\theta=H_D{}^e$, the ${}_{a_k}q_{ii}(\theta)$ become ${}_{a_k}h_{ii}{}^e$ and $P(H_D{}^e)$ becomes P_{AB}; for $\theta=H_D{}^n$, the ${}_{a_k}q_{ii}(\theta)$ become ${}_{a_k}H_{ii}{}^n$ and $P(H_D{}^n)$ becomes P; while for $\theta=1$, the ${}_{a_k}q_{ii}(\theta)$ become ${}_{a_k}N_{ii}$ and $P(1)$ becomes P. The spin function which corresponds to each one-electron orbital is written on top of the orbital, while the bracket $[\alpha\beta-\beta\alpha]$ over say electrons 11 and 12 is read as $[\alpha(11)\beta(12)-\beta(11)\alpha(12)]$. The coefficient $1/\sqrt{2}$ which appears in front of each of the $[\alpha\beta-\beta\alpha]$ bracket is already accounted for in the coefficient $\frac{1}{8}$ in front of the integral.

In a similar manner we may write the integrals ${}_{a_k}q_{ij}(\theta)$

$$
{}_{a_1}q_{13}(\theta)=\frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{2_B}(12)]^*\theta
$$

$$
\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{-2_B}(12)]\}d\tau.
$$

$$
{}_{a_2}q_{13}(\theta)=\frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{1_B}(9)\overset{\beta}{\phi}_{1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1_B}(11)\phi_{2_B}(12)]^*\theta
$$

$$
\times P(\theta)[\overset{\alpha}{\phi}_{0_A}(1)\overset{\beta}{\phi}_{0_A}(2)\overset{\alpha}{\phi}_{1_A}(3)\overset{\beta}{\phi}_{1_A}(4)\overset{\alpha}{\phi}_{-1_A}(5)\overset{\beta}{\phi}_{-1_A}(6)
$$

$$
\times\overset{\alpha}{\phi}_{0_B}(7)\overset{\beta}{\phi}_{0_B}(8)\overset{\alpha}{\phi}_{-1_B}(9)\overset{\beta}{\phi}_{-1_B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1_B}(11)\phi_{2_B}(12)]\}d\tau,
$$

$$b_1q_{13}(\theta)=\frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[\overset{\alpha}{\phi}_{0A}(1)\overset{\beta}{\phi}_{0A}(2)\overset{\alpha}{\phi}_{1A}(3)\overset{\beta}{\phi}_{1A}(4)\overset{\alpha}{\phi}_{-1A}(5)\overset{\beta}{\phi}_{-1A}(6)$$
$$\times\overset{\alpha}{\phi}_{0B}(7)\overset{\beta}{\phi}_{0B}(8)\overset{\alpha}{\phi}_{1B}(9)\overset{\beta}{\phi}_{1B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1B}(11)\phi_{2B}(12)]^*\theta \tag{2A}$$
$$\times P(\theta)[\overset{\alpha}{\phi}_{0A}(1)\overset{\beta}{\phi}_{0A}(2)\overset{\alpha}{\phi}_{1A}(3)\overset{\beta}{\phi}_{1A}(4)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1A}(5)\phi_{-2A}(6)$$
$$\times\overset{\alpha}{\phi}_{0B}(7)\overset{\beta}{\phi}_{0B}(8)\overset{\alpha}{\phi}_{1B}(9)\overset{\beta}{\phi}_{1B}(10)\overset{\alpha}{\phi}_{-1B}(11)\overset{\beta}{\phi}_{-1B}(12)]\}d\tau,$$

$$b_2q_{13}(\theta)=\frac{1}{8}\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[\overset{\alpha}{\phi}_{0A}(1)\overset{\beta}{\phi}_{0A}(2)\overset{\alpha}{\phi}_{1A}(3)\overset{\beta}{\phi}_{1A}(4)\overset{\alpha}{\phi}_{-1A}(5)\overset{\beta}{\phi}_{-1A}(6)$$
$$\times\overset{\alpha}{\phi}_{0B}(7)\overset{\beta}{\phi}_{0B}(8)\overset{\alpha}{\phi}_{1B}(9)\overset{\beta}{\phi}_{1B}(10)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{-1B}(11)\phi_{2B}(12)]^*\theta$$
$$\times P(\theta)[\overset{\alpha}{\phi}_{0A}(1)\overset{\beta}{\phi}_{0A}(2)\overset{\alpha}{\phi}_{-1A}(3)\overset{\beta}{\phi}_{-1A}(4)\overset{[\alpha\beta-\beta\alpha]}{\phi}_{1A}(5)\phi_{2A}(6)$$
$$\times\overset{\alpha}{\phi}_{0B}(7)\overset{\beta}{\phi}_{0B}(8)\overset{\alpha}{\phi}_{1B}(9)\overset{\beta}{\phi}_{1B}(10)\overset{\alpha}{\phi}_{-1B}(11)\overset{\beta}{\phi}_{-1B}(12)]\}d\tau.$$

In addition to Eqs. (1A) and (2A) we need an expression for determining the ground state energy and normalization integral for diphenyl. The following integral serves this purpose.

$$I_0(\theta)=\sum_{P(\theta)}(-1)^{P(\theta)}\int\{[\overset{\alpha}{\phi}_{0A}(1)\overset{\beta}{\phi}_{0A}(2)\overset{\alpha}{\phi}_{1A}(3)\overset{\beta}{\phi}_{1A}(4)\overset{\alpha}{\phi}_{-1A}(5)\overset{\beta}{\phi}_{-1A}(6)$$
$$\times\overset{\alpha}{\phi}_{0B}(7)\overset{\beta}{\phi}_{0B}(8)\overset{\alpha}{\phi}_{1B}(9)\overset{\beta}{\phi}_{1B}(10)\overset{\alpha}{\phi}_{-1B}(11)\overset{\beta}{\phi}_{-1B}(12)]^*\theta$$
$$\times P(\theta)[\overset{\alpha}{\phi}_{0A}(1)\overset{\beta}{\phi}_{0A}(2)\overset{\alpha}{\phi}_{1A}(3)\overset{\beta}{\phi}_{1A}(4)\overset{\alpha}{\phi}_{-1A}(5)\overset{\beta}{\phi}_{-1A}(6)$$
$$\times\overset{\alpha}{\phi}_{0B}(7)\overset{\beta}{\phi}_{0B}(8)\overset{\alpha}{\phi}_{1B}(9)\overset{\beta}{\phi}_{1B}(10)\overset{\alpha}{\phi}_{-1B}(11)\overset{\beta}{\phi}_{-1B}(12)]\}d\tau. \tag{3A}$$

For $\theta=H_D{}^e$, $P(\theta)=P$, proceeding in the usual fashion we can split off permutations confined to the A ring and also those confined to the B ring to give

$$I_0(H_D{}^e)=2E_0{}^e+h_0(H_D{}^e), \tag{4A}$$

where $h_0(H_D{}^e)$ is the same integral as (3A) with $P(\theta)=P_{AB}$ and $\theta=H_D{}^e$.

The electronic energy for the ground state of diphenyl, $E_{0D}{}^e$, is given by

$$E_{0D}{}^e=\frac{2}{N_0}E_0{}^e+\frac{1}{N_0}h_0(H_D{}^e). \tag{5A}$$

Similarly the nuclear energy is obtained from $I_0(\theta)/N_0$ by replacing θ by $H_D{}^n$ and $P(\theta)$ by P, while $N_0=I_0(1)$ where $P(1)=P$.

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The Effect of Thorium Chloride on the Potential at the Interface between Vitreous Silica and Solutions of Potassium Chloride*

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The effect of the presence of 10^{-6} *M* thorium chloride on the zeta-potential at the interface between vitreous silica and three solutions of potassium chloride has been determined by the streaming potential method. This trace of thorium changed the zeta-potential, which was strongly negative with the same solutions without added thorium, to positive values of smaller magnitude. The theory of Langmuir by which can be calculated the thickness of the wetting film owing to the zeta-potential has been extended to apply to these 4-1, 1-1 electrolyte mixtures, and the effect of this wetting film on the capillary rise of these same solutions has been studied. With only one solution (10^{-5} *M* KCl) containing added thorium was the zeta-potential low enough so that the wetting film was negligible in the capillarimeter of Jones and Ray.

INTRODUCTION

JONES and Ray[1] have accurately measured the relative surface tension of water and of solutions of electrolytes with their differential capillarimeter, and they observed that the first trace of added salt apparently decreased the surface tension below that of pure water. On the surface tension-concentration curve for potassium chloride solutions, the minimum surface tension was found at about 0.001*N* concentration, where it is 99.982 percent of the surface tension of pure water. Langmuir[2] has suggested that the minimum is not real, but is caused by variation in the thickness of the wetting film on the capillary wall, dependent on the concentration of the solution. He advanced a quantitative theory, developed more rigorously by Jones and Frizzell,[3] which gives values for the wetting film thickness large enough to decrease appreciably the effective diameter of the capillary. With a particular solution, the thickness of the film depends on the magnitude of the zeta-potential, which is the electric potential at the interface between the silica capillary and the liquid. With water and with dilute solutions the film may be several hundred angstroms thicker, if the zeta-potential is large enough, than it is with more concentrated solutions. A film of this thickness is sufficient to account for the apparent surface tension minimum observed without admitting the existence of a true minimum in the surface tension. In order to test the Langmuir theory, the zeta-potential of silica in contact with solutions of potassium chloride was measured and reported by Jones and Wood.[4] It was found that correction of the apparent relative surface tension for the thickness of the wetting film as computed by the Langmuir equation eliminated the minimum in the surface tension-concentration curve.

An earlier test of the Langmuir theory was made by Jones and Frizzell,[3] but their results were inconclusive. Langmuir[2] had suggested that if the zeta-potential were to be lowered to zero, or nearly so, by the addition of thorium ions, the film thickness should be decreased, and the minimum eliminated. The best evidence, according to Abramson,[5] indicated that the zeta-potential of glass was near zero in a solution of 10^{-6} *M* thorium ion. No similar information existed regarding silica. Jones and Frizzell made numerous measurements of the relative surface tensions of thorium chloride solutions in the concentration range 10^{-9} to 5×10^{-5} *M*, but were unable to deduce from these measurements the particular concentration at which the zeta-potential of silica was zero. They stated that direct

* Contribution from the Mallinckrodt Chemical Laboratory of Harvard University.

[1] Grinnell Jones and Wendell A. Ray, J. Am. Chem. Soc. **59**, 187 (1937); **63**, 288 (1941); **63**, 3262 (1941); **64**, 2744 (1942).

[2] Irving Langmuir, Science **88**, 430 (1938); J. Chem. Phys. **6**, 873 (1938).

[3] Grinnell Jones and Laurence D. Frizzell, J. Chem. Phys. **8**, 986 (1940).

[4] Grinnell Jones and Lloyd A. Wood, J. Chem. Phys. **13**, 106 (1945).

[5] H. A. Abramson, *Electrokinetic Phenomena* (Chemical Catalog Company, New York, 1934), p. 186.

TABLE I. Zeta-potentials (millivolts) with 1.0×10^{-6} M $ThCl_4-1.00\times10^{-5}$ M KCl.

Time (days)	Number of measurements	κ ($\times10^6$) (av)	E/P (av)	ζ (mv)	Average deviation
		Capillary I			
2	4	2.035	56.3	−11.1	0.6 mv
3	16	2.252	31.1	−6.8	2.0
4	8	2.208	33.5	−7.1	1.5
8	8	2.211	19.6	−4.4	1.0
9	8	2.246	96.2	−20.9	1.7
10	8	2.284	86.7	−19.1	1.3
16*	8	2.102	69.2	+14.1	0.7
17	8	2.032	35.8	+7.0	1.0
18	8	2.078	52.0	+10.4	1.4
		Capillary II			
2	4	2.185	175	+37.1	4.8
3	16	2.254	161.7	+39.9	0.8
4	8	2.426	146.7	+34.4	0.7
8	8	2.249	134.0	+33.0	2.6
9	8	2.718	136.3	+35.7	1.9
10	8	2.766	140.3	+37.5	2.0
16*	8	2.454	128.9	+30.5	1.1
17	8	2.273	82.9	+18.2	0.7
18	8	2.412	101.2	+23.6	1.1

* Preceding this set of measurements, a new sample of solution was put in the apparatus, as it was supposed that thorium may have been lost from the solution in apparatus I, due perhaps to adsorption.

measurement of the zeta-potential was needed to settle this question. However, they redetermined the apparent relative surface tension of potassium chloride solutions, using 10^{-6} M thorium chloride solution as the solvent component rather than pure water, on the presumption that if the minimum were eliminated, it would be evident that the addition of thorium had decreased the zeta-potential enough so that the wetting film was negligible, and that Langmuir's theory was correct. They found that the minimum was not eliminated, although it was not as pronounced as without the thorium. The question then arose as to whether the zeta-potential was brought near enough to zero by the added thorium, and the work herein reported was undertaken to provide an answer. The zeta-potential of silica in contact with solutions of 10^{-5}, 10^{-4}, and 10^{-3} M potassium chloride, each 10^{-6} M in thorium chloride, has been determined by the measurement of streaming potentials.

EXPERIMENTAL

The streaming potential apparatus has been fully described in an earlier publication,[4] and in obtaining the measurements reported below, no changes were made either in the apparatus or in the experimental procedure.

Thorium chloride was prepared following the method described by Jones and Frizzell.[3] A solution of 0.020 M concentration was prepared with conductivity water and stored in a non-sol glass bottle. No turbidity appeared on long standing. The 10^{-6} M solutions were prepared by dilution of this stock solution. The potassium chloride was recrystallized from analytical reagent KCl, and the solid was weighed out for addition to the proper quantity of the 10^{-6} M thorium chloride solution. Conductivity water from a still with block tin condensers was used in preparing the solutions, and when freed from carbon dioxide, had a specific conductance of less than 0.8×10^{-6} mho per cm. The solutions used were made up in contact with laboratory air, but after the solutions were put in the streaming potential apparatus, carbon dioxide-free air was bubbled through them until the dissolved carbon dioxide was removed.

In referring to these solutions in the discussions following, it will be considered sufficient for the sake of brevity to refer only to the KCl concentrations, with the understanding that each contains 1.0×10^{-6} M thorium chloride in addition. The temperature in all experiments was 25°C $\pm0.03°$.

The first solution measured was 1.00×10^{-5} KCl and the results obtained are given in Table I. The "Time" is the number of days that the solution had been in contact with the capillary when the given measurement was made. The "Number of measurements" gives the number of individual streaming potential measurements which were averaged to give the reported values of κ and E/P. κ is the effective specific conductance of the liquid in the capillary, and includes any contribution of surface conductance. E/P is the ratio of the streaming potential E to the pressure P which produced it. ζ is obtained from the equation of Helmholtz[6]

$$\zeta=(4\pi\eta E\kappa)/(DP),$$

in which η is the viscosity of the solution and D is the average dielectric constant of the liquid in the ionic double layer. Both these quantities are

[6] H. Helmholtz, Wied. Ann. 7, 337 (1879).

assumed to be the same as those for pure water ($\eta = 0.00895$ and $D = 78.49$, according to Dorsey).[7] It should be mentioned that the values given for ζ were obtained by taking the average of the ζ's obtained from each individual measurement of κ and E/P, so that in general the ζ given is slightly different from what would be obtained by using the average values of κ and E/P for computing it.

When the first measurement was made, after the solution had been in contact with the capillary for two days, the zeta-potential of capillary I (diameter: 0.032 cm) was found to be -11 mv and that of capillary II (diameter: 0.017 cm) was $+37$ mv. The zeta-potential varied somewhat during the succeeding eight days, but it was apparent that the potentials of the two capillaries were not reaching agreement. These results seemed to indicate that the concentration of the thorium might have changed in one or both sets of apparatus, perhaps owing to unequal amounts of adsorption of the thorium on the walls. Therefore, both were refilled with a second portion of the solution. The capillaries were not disturbed. It was then observed that the zeta-potential of both capillaries was positive although not yet in very good agreement. These values are given in Table I beginning 16 days after this solution first came in contact with the capillary. Inasmuch as there was nothing to indicate that any one of the zeta-potentials obtained on the 16th, 17th, and 18th days was more probable than another, the average of these six values was accepted as the most probable value. This accepted value is $+17$ mv and the probable error of a single measurement is ± 6 mv. The addition of 1.0×10^{-6} M thorium chloride to the 10^{-5} M potassium chloride has thus reversed the polarity of the zeta-potential and greatly decreased the magnitude, changing it from -148 mv, reported earlier,[4] to about $+17$ mv.

The next solution measured was 1.000×10^{-4} M KCl, also with 1.0×10^{-6} M $ThCl_4$. The capillaries were treated with boiling aqua regia, and thoroughly rinsed and steamed with conductivity water. The other parts of the apparatus were rinsed thoroughly with the solution, but not with acid or water, to avoid removal of the thorium ions which may have been adsorbed on the walls while the previous solution was in them. The presumption was that while the relatively small surface of the capillary walls would not adsorb enough thorium to change the concentration appreciably, the much larger surfaces of the other parts of the apparatus might do so, as they evidently did with the 10^{-5} M KCl solution. Whether this was true or not, the difficulties encountered with the first solution did not arise again. A summary of the zeta-potential measurements with the 10^{-4} M KCl solution is given in Table II, and it will be seen that the potentials observed were in better agreement than with the 10^{-5} M solution. After five days, the potentials of the two capillaries were 4 mv apart, and the accepted value was $+57$ mv, the average of these. The addition of the thorium has thus changed the zeta-potential from -135 to about $+57$ mv for silica in contact with 10^{-4} M KCl.

Following this series, the apparatus was thoroughly cleaned to remove the thorium. After repeated treatment of the capillaries with aqua regia, concentrated nitric acid, and hot saturated KCl solution, zeta-potential values of -145 mv for capillary I and -140 mv for capillary II were obtained with 1.000×10^{-4} M KCl without added thorium. This demonstrated that the thorium ions could be and were removed from the capillary surface, and that the surface was substantially the same as it was before it came in contact with the thorium, when -135 mv was obtained with the same solution.

TABLE II. Zeta-potentials (millivolts) with 1.0×10^{-6} M $ThCl_4$ – 1.000×10^{-4} M KCl.

Time (days)	Number of measurements	κ ($\times10^6$)	E/P (av)	ζ (mv)	Average deviation
		Capillary I			
1	4	16.24	34.06	+53.4	0.1 mv
2	8	16.04	33.23	+51.5	0.2
3	8	16.06	31.73	+49.2	0.2
4	8	16.14	32.54	+50.8	0.7
5	8	16.15	35.29	+55.1	0.2
		Capillary II			
1	4	16.42	45.28	+71.8	0.4
2	8	16.23	40.64	+63.7	0.5
3	8	16.27	39.54	+62.1	0.2
4	8	16.35	37.81	+59.7	0.1
5	8	16.36	37.49	+59.2	0.5

[7] N. E. Dorsey, *Properties of Ordinary Water-Substance* (Reinhold Publishing Corporation, New York, 1940), pp. 187 and 364.

Then the third solution with added thorium, 1.00×10^{-3} M KCl and 1.0×10^{-6} M $ThCl_4$, was placed in the apparatus. The various parts were of course thoroughly rinsed with the solution before assembly. Table III gives the average zeta-potentials, and the accepted value was +67 mv, the average of the last pair of measurements, which were closest together. The addition of the thorium has therefore changed the zeta-potential of the 10^{-3} M KCl solution from −112 to about +67 mv.

With none of these solutions was the study of the change of the zeta-potential with time carried on as long as with the KCl solutions reported earlier because the purpose here was to obtain an idea of the value of the zeta-potential as it most probably was in the surface tension capillarimeter. Since it is well established that a considerable period of time is usually necessary for an equilibrium potential to be obtained, and inasmuch as the solutions were not continuously in contact with the surface tension capillarimeter as long as these were with the streaming potential apparatus, the zeta-potentials reported here are probably only an approximation to what they were in the experiments of Jones, Ray, and Frizzell.

The chief experimental difficulty seemed to be in maintaining the thorium ion concentration at 10^{-6} M, observed in the experiments with the 10^{-5} M KCl. Although there was no difficulty in preparing the solution, it is inevitable that some adsorption of thorium must occur at all the surfaces of the containing vessels, since thorium must be adsorbed rather strongly to be capable of so great an effect on the zeta-potential. Even though there may be actually only a small amount of thorium removed from the solution by adsorption, this small quantity may be an appreciable fraction of the thorium in the 10^{-6} M solution. This probably explains the lower order of accuracy of the measurements with the solutions containing 10^{-6} M thorium chloride than was obtained in the measurements reported earlier.[4]

However, it is reasonable to assume that the zeta-potentials measured in the streaming potential apparatus are essentially the same as they were in the surface tension capillarimeter with the same solutions, and the Langmuir theory will be applied using these data.

TABLE III. Zeta-potentials (millivolts) with 1.0×10^{-6} M $ThCl_4$ − 1.000×10^{-3} M KCl.

Time (days)	Number of measurements	κ ($\times10^6$)	E/P (av)	ζ (mv)	Average deviation
		Capillary I			
1	8	148.36	5.117	+73.3	0.3 mv
2	8	148.31	5.088	+72.9	0.7
3	8	148.30	5.064	+72.5	0.1
4	8	148.25	4.865	+69.7	0.8
		Capillary II			
1	8	147.68	4.610	+65.8	0.8
2	8	147.69	4.554	+65.0	0.8
3	8	147.75	4.527	+64.6	0.4
4	8	147.72	4.510	+64.2	0.7

It is evident that the 10^{-6} M thorium chloride has not caused the zeta-potential of the silica with these solutions to become zero, but it has gone further and made the potential positive. A lower concentration of thorium would probably suffice to bring the potential to zero. Further experimental work is needed to determine exactly what this concentration would be, but it is apparent that only a slightly lower thorium concentration would be needed for the 10^{-5} KCl solution. Since the zero potential was overshot by a much larger margin for the 10^{-4} and 10^{-3} M KCl solutions, it seems probable that a concentration of thorium much lower than 10^{-6} would be enough to reduce the potential just to zero with these solutions. It seems reasonable to conclude that a different thorium concentration will be needed for each of these solutions to bring about a zero potential, because it is evident that less thorium would be required to reduce the potential of −112 mv of the 10^{-3} M KCl to zero than the greater potential of −148 mv for the 10^{-5} M KCl. Therefore, a series of solutions with different thorium concentrations with each of the KCl solutions will have to be measured in the streaming potential apparatus, and when the proper amount of added thorium to produce a zeta-potential of zero is ascertained, the surface tension measurements will need to be repeated on the proper solutions. The extreme dilution of the thorium with the attendant dangers of adsorption on the walls discussed above gives rise to the idea that a trivalent positive ion might be used more conveniently instead of thorium.

However, according to the Langmuir theory, it

is not necessary for the zeta-potential to be reduced exactly to zero for the wetting film to be very thin. Langmuir considers the film to be attributed to the fact that the potential on the wall of the capillary causes a distribution of the ions in the solution such that the osmotic pressure of the water in the film is less than it is in the bulk of the solution. If the potential is high enough, the difference in osmotic pressure becomes sufficient to create a thick film. As will be made clear below, there is a certain value of the zeta-potential for each solution which must be attained or exceeded before the difference in osmotic pressure becomes large enough to begin the formation of a thick wetting film on the capillary wall. If the zeta-potential is below this critical value, the wetting film will be attributed only to van der Waals or other short range forces. It will be shown below that the zeta-potential of the 10^{-5} M KCl solution was converted by the thorium to a low enough value so that the wetting film vanished, as far as the zeta-potential contribution was concerned, but that with the other two solutions, the potential was great enough so that the wetting film was appreciable. Therefore, it is evident that the thorium has not reduced the wetting film to zero, except for the 10^{-5} M KCl solution.

However, Jones and Wood[4] found that application of the Langmuir correction to the surface tension measurements, using the zeta-potential data, eliminated the minimum in the surface tension curve for the KCl solutions. Since the zeta-potentials for these same solutions with added thorium are now determined with sufficient accuracy, the Langmuir theory can again be tested by application of the correction to the surface tension data on these solutions. It is true that it would have been perhaps a neater test had the thorium concentration been such as to cause the wetting film to vanish, but since the thickness of the wetting film can be calculated according to Langmuir's quantitative theory, a second critical test can be made with the zeta-potentials reported above.

APPLICATION OF THE LANGMUIR THEORY

Jones and Frizzell developed Langmuir's theory only for a 1–1 electrolyte, so it is necessary to generalize their treatment somewhat to apply it to a mixture of electrolytes. Therefore, we begin with the general Poisson-Boltzmann equation for the electric potential in an electrolyte solution in the region of a charged plane instead of the equation for a 1–1 electrolyte:

$$\frac{d^2\psi}{dx^2}=\frac{-4\pi}{D}\sum_{i=1}^{s} n_i z_i \epsilon \exp\left(\frac{-z_i\psi\epsilon}{kT}\right), \qquad (1)$$

where ψ is the positive electric potential, D is the dielectric constant of the solution, n_i is the number of ions of species i per cc, z_i is the charge on an ion of species i, and ϵ is the magnitude of the electronic charge. $d^2\psi/dx^2$ is used instead of $\nabla\psi$ since the potential is assumed to vary only in the direction perpendicular to the planar interface. This equation is conveniently simplified by the following substitutions:

$$\begin{aligned} &\eta \equiv \epsilon\psi/kT, \\ &\theta \equiv \kappa x, \\ &\kappa \equiv \left[(4\pi\epsilon^2/DkT)\sum_{i=1}^{s} n_i z_i^2\right]^{\frac{1}{2}}, \\ &1/A \equiv \sum_{i=1}^{s} n_i z_i^2, \\ &p \equiv \frac{d\eta}{d\theta}. \end{aligned} \qquad (2)$$

Equation (1) then becomes

$$p\frac{dp}{d\eta}=-A\sum_{i=1}^{s} n_i z_i \exp(-z_i\eta), \qquad (3)$$

which on integration gives

$$p^2=(2A\sum_{i=1}^{s} n_i \exp(-z_i\eta))+C. \qquad (4)$$

To evaluate the constant of integration, C, we follow Langmuir and Jones and Frizzell, who say that at the air interface of the film when $\theta=0$, the potential is at a minimum, so that $\eta=m$, and $p=0$. The value of C is then

$$C=-2A\sum_{i=1}^{s} n_i \exp(-z_i m). \qquad (5)$$

Combining Eqs. (4) and (5) and rearranging, we have

$$\frac{d\theta}{d\eta}=\frac{1}{[2A\sum_{i=1}^{s}(\exp(-z_i\eta)-\exp(-z_im))]^{\frac{1}{2}}}. \quad (6)$$

Since there is no known integral of this expression, the general case can be carried no further. We now make the substitutions

$$K=e^{-m},\qquad y=e^{-\eta}, \quad (7)$$

and Eq. (6) becomes

$$\frac{d\theta}{dy}=\frac{-1}{[2Ay^2\sum_{i=1}^{s}n_i(y^{z_i}-K^{z_i})]^{\frac{1}{2}}}. \quad (8)$$

It is now evident that if z_i has integral values from -2 to $+2$, Eq. (8) can be expressed as an elliptic integral.[8] However, if any z_i is an integer greater in absolute value than 2, as with thorium ion, which has a charge of $+4$, Eq. (8) is than a hyperelliptic integral and cannot be integrated explicitly. It will be shown that a close approximation for Δr, the thickness of the wetting film, can be obtained even so.

Let

Th^{+4} be species 1: $z_1=+4$;
K^+ and H^+ be species 2: $z_2=+1$;
Cl^- and OH^- be species 3: $z_3=-1$.

Substituting these values in Eq. (8), and also recalling that $n_i=c_iN\times10^{-3}$, where c_i is the ionic concentration and N is Avogadro's number, we then have for the solution of thorium chloride and potassium chloride

$$\frac{d\theta}{dy}=\frac{-(10c_1+c_2)^{\frac{1}{2}}}{(c_2)^{\frac{1}{2}}[(c_1/c_2)y^6+y^3+(c_3/c_2)y-(c_1K^4+c_2K+c_3K^{-1})y^2/c_2]^{\frac{1}{2}}}. \quad (9)$$

It is evident that

$$\kappa\cdot\Delta r=\int_{y_0}^{y_1}d\theta$$

where Δr is the thickness of the wetting film, measured from the air interface in the direction of the wall; $y_0=K$, the value of y at the air interface; and y_1 is the value of y when $\psi=\zeta$.

Before proceeding further with Eq. (9), a digression will be made in order to find out how values of K are determined. Langmuir postulates that there is an equilibrium between three forces at the air-solution interface, provided that the film thickness is sufficiently large so that van der Waals or other short range forces do not play an important role in determining the thickness. The three forces in equilibrium at the level of the capillary meniscus are (1) the negative pressure, $-(d-\beta)hg$, tending to make the film thinner, owing to the force of gravity g, h being the capillary rise, d the density of the solution, and β the density of air; (2) the pressure $(d-\beta)hg/2$, owing to the surface tension of the cylindrical surface, tending to make the film thicker; and (3) the difference in osmotic pressure between the bulk solution and the air-solution interface of the wetting film. The osmotic pressure is determined from van't Hoff's simple law: $P=nkT$, where n is the total number of ions per cc. At the air interface of the film, n is obtained from the Maxwell-Boltzmann equation: $n=\sum_i n_i\exp(-z_i\epsilon\psi/kT)$ or $n=\sum_i n_iK^{z_i}$ at the air interface. The osmotic pressure in the bulk solution is $P=\sum_i n_ikT$. The difference in osmotic pressure, tending to make the film thicker, is then

$$\sum_i n_ikT(K^{z_i}-1).$$

Combining these pressures at equilibrium, when their sum is zero,

$$\sum_i n_ikT(K^{z_i}-1)-(d-\beta)hg/2=0. \quad (10)$$

For thorium chloride-potassium chloride mixtures, Eq. (10) becomes after subtituting $n_i=c_iN\times10^{-3}$ for $i=1, 2, 3$:

$$\frac{c_1+c_2+c_3}{c_2}+\frac{500(d-\beta)hg}{c_2NkT}=\frac{c_1}{c_2}K^4+K+\frac{c_3}{c_2}K^{-1}\equiv2\lambda. \quad (11)$$

K is then determined by solving this equation for its root between 0 and 1, since $0<K<1$ if the zeta-potential is positive. The value computed for

[8] The reduction of such expressions to the Legendrian form is discussed in J. Edwards, *The Integral Calculus* (Macmillan and Company, Ltd., London, 1922), Vol. II, p. 578 and following.

K corresponds to a certain ψ_m at the air interface, which is the minimum ψ in the film. This means that if the potential ψ due to the zeta-potential is sufficiently high so that enough ions are attracted into the film to make the osmotic pressure difference large enough to overcome the pressure $-(d-\beta)hg/2$, then the value of ψ at the air interface is ψ_m, which can then be computed according to Eq. (10). Obviously ζ must be larger than the computed ψ_m for this to be possible. If ζ is found experimentally to be smaller than ψ_m, then there can be no wetting film attributed to the zeta-potential, because the osmotic pressure is insufficient to form it.

In proceeding with Eq. (9), substitute 2λ as expressed in Eq. (11), and make the following further simplifications of notation:

$$\begin{aligned} &\mu \equiv c_3/c_2; \qquad B \equiv [(10c_1+c_2)/c_2]^{\frac{1}{2}}; \\ &b \equiv (c_1/c_2)y^6; \quad a \equiv y^3-2\lambda y^2+\mu y. \end{aligned} \tag{12}$$

Thus Eq. (9) becomes

$$(d\theta/dy) = -B/[a+b]^{\frac{1}{2}}. \tag{13}$$

In the region of convergence, this equation can now be expanded into a Taylor series:

$$\frac{d\theta}{dy} = \frac{-B}{\sqrt{a}}\left[1-\frac{b}{2a}+\frac{3\cdot 1}{2!2^2}\left(\frac{b}{a}\right)^2 - \cdots + (-1)^n \frac{(2n-1)(2n-3)\cdots 1}{n!2^n} \times \left(\frac{b}{a}\right)^n \cdots\right] \equiv \frac{-BS(y)}{\sqrt{a}}. \tag{14}$$

This series, represented by $S(y)$, is uniformly convergent in the region where $|b|<|a|$, and in this region is therefore integrable termwise. To determine whether the limits between which we wish to integrate lie within this region, we examine first the limit $y_0=K$, determined by Eq. (11), which can be rewritten as

$$-\frac{c_1}{c_2}K^5 = K^2-2\lambda K+\mu. \tag{15}$$

Compare this with the requirement for convergence of the series, and we see immediately that $|b|=|a|$ when $y=K$, and $|b|<|a|$ when $y<K$. Therefore the series is not convergent at $y=K$, although it is convergent for any y less than K. Let $y_0=K-\epsilon$ and let ϵ be taken so small that any error introduced by using this y_0 instead of K becomes infinitesimal. If the values of y in the region of integration are restricted to $0<y_1\leq y\leq y_0$, which is also a requirement of the physical assumption $|\psi_m|<|\zeta|$ of the theory, they are all in the region of convergence, the series expansion is valid, and Eq. (14) is integrable termwise.

This integration would be extremely laborious to perform, and fortunately is unnecessary, since an idea of the value of the integral can be had by a relatively simple method. The series $S(y)$ in Eq. (14) will have its minimum value in its convergent region at y_0 when b/a has its greatest value, slightly less than unity. Its maximum value is at y_1, where b/a is very small, and $S(y_1)$ is slightly less than unity if y_1 is appreciably smaller than y_0. The value of the series can be said to be $S(y_0)\leq S(y)<1$ for all values of y in $y_1\leq y\leq y_0$. The sum of the first 15 terms of $S(y_0)$ is 0.78053, and the 16th term is -0.13825. In a uniformly convergent, alternating series, the value of the remainder of the series after summation of the first n terms will be of the same sign as, and less in absolute value than the $(n+1)$st term. Thus we can say[9]

$$\int_{y_1}^{y_0}\frac{dy}{\sqrt{a}} > \int_{y_1}^{y_0}\frac{S(y)dy}{\sqrt{a}} > 0.64\int_{y_1}^{y_0}\frac{dy}{\sqrt{a}}. \tag{16}$$

However, the spread between the right and left members of (16) can be narrowed considerably by considering the integration to be performed in two steps: first between y_1 and an intermediate value y_i, and then between y_i and y_0, where y_i is defined by

$$\frac{|b|}{|a|} = \frac{1}{100}; \quad y_1<y_i<y_0. \tag{17}$$

[9] Should it occur to the reader that the limits of the integrals appear to be reversed for a correct statement of the inequality, it should be mentioned that $\int_{y_0}^{y_1} dy/\sqrt{a}$ is negative when $y_1<y_0$. This is demonstrated below when it is resolved into the Legendrian form of an elliptic integral (Eq. (22)), and it is also required by the physical nature of the problem since $\Delta r \equiv x_1-x_0 = \frac{-B}{\kappa}\int_{y_0}^{y_1}\frac{dy}{[a+b]^{\frac{1}{2}}}$ wherein Δr must be positive. Actually the question of sign is immaterial, since the proper sign of the square root may be taken to give a positive Δr.

Now the minimum value of the series $S(y)$ in the interval y_1 to y_i is at $y=y_s$, where $|b|/|a|=1/100$, and evaluation of the first three terms tells us

$$\int_{y_1}^{y_i}\frac{S(y)dy}{\sqrt{a}}>0.995\int_{y_1}^{y_i}\frac{dy}{\sqrt{a}}. \tag{18}$$

Then from (17) and (19) we have

$$\int_{y_1}^{y_0}\frac{dy}{\sqrt{a}}>\int_{y_1}^{y_0}\frac{S(y)dy}{\sqrt{a}}>0.995\int_{y_1}^{y_i}\frac{dy}{\sqrt{a}}+0.64\int_{y_i}^{y_0}\frac{dy}{\sqrt{a}}. \tag{19}$$

It is perhaps worthwhile to point out that the reasoning between Eqs. (13) and (19) merely constitutes a rigorous proof, when the numerical values for the solutions of present interest are applied, as will be shown, that the y^6 term in Eq. (9) can be neglected without introducing a large error. It also makes possible the calculation of two numbers between which Δr must lie, and it will be shown that these numbers are relatively close together.

It remains to express $\int dy/\sqrt{a}$ in a form which can be evaluated.

Let

$$y=[(\sqrt{\mu})(1-t)]/(1+t),$$
$$\mu<\lambda\sqrt{\mu}. \tag{20}$$

The integral then reduces to the Legendrian form of an elliptic integral, and we have

$$-B\int_{y_0}^{y_1}\frac{dy}{\sqrt{a}}=H\int_{t_0}^{t_1}\frac{dt}{[-(1-t^2)(1-q^2t^2)]^{\frac{1}{2}}} \tag{21}$$

TABLE IV. Calculation of parameters, and y_i, K and ψ_m.

KCl concentration	10^{-3}	10^{-4}	10^{-5}
$c_1(\times 10^6)$	1	1	1
$c_2(\times 10^6)$	1002	102	12
$c_3(\times 10^6)$	1006	106	16
$d-\beta$	0.995,95	0.995,91	0.995,90
$(1/\kappa)(\times 10^8)$	95.62	287.5	649.1
μ	1.004,00	1.039,22	1.333,33
B	1.005,0	1.048,9	1.354,0
λ	1.109,28	2.073,50	10.125,0
H	4.339,25	1.444,81	0.639,34
q	4.436,11	1.712,96	1.121,36
α	76.972°	54.283°	26.903°
y_i	0.623,00	0.267,60	0.066,05
K	0.633,46	0.267,92	0.066,06
m	0.456,56	1.317,08	2.717,19
ψ_m (mv)	+11.73	+33.83	+69.79
ζ (experimental)	+67	+57	+17

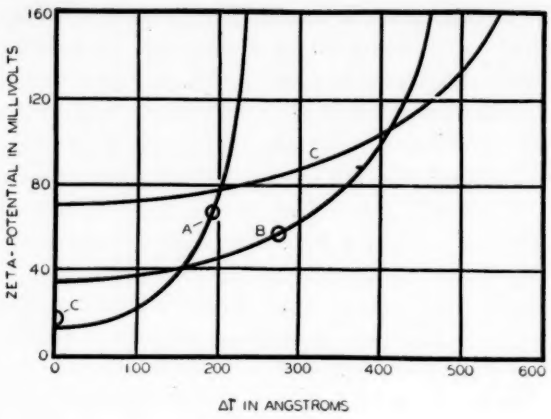

FIG. 1.

where

$$-q^2\equiv\frac{\mu+\lambda\sqrt{\mu}}{\mu-\lambda\sqrt{\mu}},$$
$$H\equiv\frac{2B\sqrt{\mu}}{\{2(\sqrt{\mu})[\lambda(\sqrt{\mu})-\mu]\}^{\frac{1}{2}}}.$$

To convert this into the form in which Legendre's tables of elliptic functions can be used, change the variable again by the substitution

$$q^2t^2=q^2\cos^2\phi+\sin^2\phi,$$

and we have

$$-B\int_{y_0}^{y_1}\frac{dy}{\sqrt{a}}=\frac{-H}{q}\int_{\phi_0}^{\phi_1}\frac{d\phi}{[1-\sin^2\alpha\sin^2\phi]^{\frac{1}{2}}}=\frac{-H}{q}[F(\alpha,\phi_1-F(\alpha,\phi_0)], \tag{22}$$

in which $\sin^2\alpha=(q^2-1)/q^2$. Thus we have evaluated Δr as being confined between two readily evaluated integrals:

$$\frac{H}{\kappa q}[F(\alpha,\phi_0)-F(\alpha,\phi_1)]>\Delta r>\frac{H}{\kappa q}[0.995\{F(\alpha,\phi_i)-F(\alpha,\phi_1)\}+0.64\{F(\alpha,\phi_0)-F(\alpha,\phi_i)\}]. \tag{23}$$

COMPUTATION OF Δr

In computing Δr it is necessary to determine the various constants and the limits of integration defined in the above equations. These depend on

the concentrations of the different ions (c_1, c_2, c_3), the capillary rise (h), and the density in air of the solution ($d-\beta$), all of which depend on the particular solution. The temperature was 25°C in all cases. The fundamental physical constants required are taken from the tabulation of Birge.[10] The concentration of the thorium ion (c_1) is the same in all solutions: 1.0×10^{-6} M. The concentration c_2 is the sum of the concentrations of all ions having a charge of $+1$, in these instances, of potassium and hydrogen, the latter caused by the ionization of water. It is assumed that all ions derived from water are univalent, and that since the specific conductance of the water used was about 0.8×10^{-6}, the concentrations of positive and negative ions from the water are each 2×10^{-6} M (considering Λ, the equivalent conductance to be 400). For example, c_2 for the solution of 10^{-4} M KCl is 102×10^{-6}. The concentration c_3 is the sum of the concentrations of ions of -1 charge, namely, the chloride from both KCl and $ThCl_4$, and hydroxide from water. As an illustration, c_3 for the solution with 10^{-4} KCl is 106×10^{-6}. The capillary rise h is taken as 10.862 cm in each case, and the dielectric constant D is 78.49.

In Table IV are given numerical values of the various quantities required for the computation of Δr, according to the definitions given above. Solution of Eq. (17) gives y_i (actually the y_i values give $|b|/|a|$ somewhat smaller than 0.01); solution of Eq. (11) gives K; and ψ_m, the potential at the air-solution interface, is given by $m=\epsilon\psi_m/kT$. The experimental values for ζ are given for comparison with ψ_m, and it should be noted that for the 10^{-5} M KCl solution the experimental value of ζ is less than ψ_m, which is assumed to be the minimum value in the film. This means that the theory is not applicable to this solution, since the thorium ion has evidently reduced the zeta-potential to such a low value that it is no longer an important factor in determining the film thickness. For this solution, the film would presumably be negligible and attributed to van der Waals or other adsorptive forces operating at short range of a few angstroms. The inapplicability of the Langmuir theory to this solution should not be regarded as a weakness of the theory, but rather as the achievement of the result intended by Langmuir when he proposed the addition of thorium to reduce the zeta-potential to such a low value that it would not create a thick film.

Using the values of the parameters in Table IV, the thickness of the film has been calculated for various values of the zeta-potential, and the curves described have been plotted in Fig. 1. The curves A, B, and C are for the solutions containing 10^{-3}, 10^{-4}, and 10^{-5} M KCl, respectively. The values plotted are the "upper bound" of Δr, the left member of (23). The "lower bound," or right member of (23) is at most 9 angstroms less than the given Δr values. This demonstrates that the approximate value obtained for the hyperelliptic integral in Eq. (9) is satisfactory for application of the Langmuir correction. The experimental values obtained for ζ are shown on the curves A and B by circles, and the half-circle marked C, on the ordinate axis, represents the experimental ζ obtained for the solution with 10^{-5} M KCl. This point is really not off the curve C, because these curves should all be considered as starting at the origin. Thus as ζ increases from 0 to ψ_m, Δr is always 0, according to the Langmuir theory, and when ζ increases beyond ψ_m, Δr

TABLE V. Wetting film thicknesses.

KCl concentration: $10^{-3}M$				
ζ			+67	$+\infty$
η			2.608,645	∞
y_1			0.073,635	0
y_i		0.623,00		
$y_0(=K)$	0.633,46			
t	0.225,343	0.233,231	0.863,086	1
$\sin\phi$	1.0000	0.998,11	0.518,401	0
ϕ	90.00°	86.475°	31.225°	0°
$F(\alpha,\phi)$	2.900,60	2.630,64	0.572,46	0
$F(\alpha,\phi_0)-F(\alpha,\phi_1)$		0.269,96	2.328,14	2.900,60
Upper bound, Δr (angstroms)		22.5	194.5	242.3
Lower bound, Δr		14.4	185.4	233.0
KCl concentration: 10^{-4}				
ζ			+57	$+\infty$
η			2.219,295	∞
y_1			0.108,684	0
y_i		0.26760		
$y_0(=K)$	0.26792			
t	0.583,762	0.584,156	0.807,316	1
$\sin\phi$	1.0000	0.999,670	0.726,831	0
ϕ	90.00°	88.530°	46.622°	0°
$F(\alpha,\phi)$	2.019,34	1.975,28	0.876,40	0
$F(\alpha,\phi_0)-F(\alpha,\phi_1)$		0.044,06	1.142,94	2.019,34
Upper bound, Δr (angstroms)		10.7	277.2	489.7
Lower bound, Δr		6.8	271.9	483.4

[10] R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941).

increases according to the abscissas of the curves shown.

Examples of the computations are given in Table V, for the "upper" and "lower bounds" of Δr (i.e., the left and right members of (23)). These are given for the experimental values of ζ and for infinite ζ for the 10^{-3} and 10^{-4} M solutions. The upper and lower bounds for Δr for infinite ζ for the 10^{-5} M solution are 615 and 610 angstroms, respectively, determined in the same manner as in Table V.

HYDROLYSIS OF THORIUM CHLORIDE

The application of the Langmuir theory given above is based on the simplifying assumption that thorium chloride is not hydrolyzed. This is unquestionably an over-simplification, as there is no doubt that it does hydrolyze appreciably in water, because its solutions are acidic. It is possible that there may exist in solution the ions Th^{+4}, $Th(OH)^{+3}$, $Th(OH)_2^{+2}$, and $Th(OH)_3^{+}$, and there may be other ions of thorium as well. There is no quantitative information in the literature on this hydrolysis. Experiments are in progress in this laboratory to determine the extent of hydrolysis, and until they are completed, there is no way of making a precise computation of the thickness of the wetting film taking this into account. However, it is evident that Δr would be little affected even by relatively complete hydrolysis, because the concentration of potassium chloride is greater than that of the thorium chloride. Without attempting to discuss in detail the necessary alterations in the mathematical treatment to take hydrolysis into account, it can be stated that the effect is to shift the curves A, B, and C in Fig. 1 a short distance in the direction of greater concentration. Thus C would be shifted slightly in the direction of B, and B slightly in the direction of A, while A would be scarcely changed since the potassium chloride concentration is so very much larger than the thorium chloride concentration. With complete hydrolysis to $Th(OH)_3^{+}$ or $Th(OH)_4$, the computation would revert to the simple 1–1 electrolyte case in which $c=[KCl]+4\times10^{-6}$, (or $c=[KCl]+6\times10^{-6}$, taking into account the ions from the water). It is therefore evident that even if the information were available to take the hydrolysis into account, the curves A, B, and C would be essentially unchanged.

APPLICATION OF THE WETTING FILM CORRECTION TO THE SURFACE TENSIONS

The wetting film correction factor to be applied to the apparent relative surface tension is $(r-\Delta r_c)/(r-\Delta r_0)$ where r is 0.0136 cm, the radius of the capillary. The surface tension of 10^{-3} M KCl with 10^{-6} M $ThCl_4$ is taken as the average of the two values given by Jones and Frizzell, and Dr. W. A. Ray kindly measured the surface tension of 10^{-4} and 10^{-5} M KCl with added thorium for the writer. His previously unpublished results are given in Table VI, along with the Jones-Frizzell measurement, and are referred to 10^{-6} M $ThCl_4$ instead of pure water. Since the zeta-potential of the reference solution has not been measured, the Langmuir correction is here applied with reference to the 10^{-5} M solution, and the corrected surface tensions are relative to this solution. If the minimum is eliminated, the surface tensions of the 10^{-3} and 10^{-4} M solutions should be greater than (or equal to) that of the 10^{-5} M solution, but it is seen in Table VI that on the contrary the application of the correction serves to lower the minimum. These results then do not support Langmuir's suggestion that there is no minimum in the curve.

It is worthwhile to inquire what the film thicknesses would have to be for the Langmuir correction to eliminate the minimum, in order to see whether experimental error in the zeta-potential measurements might account for the failure of the theory. Rearranging the equation

$$\sigma_R=\sigma_E\frac{r-\Delta r_c}{r-\Delta r_0},$$

where σ_R is the corrected relative surface tension, and σ_E is the observed apparent relative surface tension, we have

$$\Delta r_c-\frac{\sigma_R}{\sigma_E}\Delta r_0=\left(1-\frac{\sigma_R}{\sigma_E}\right)r.$$

Since σ_R/σ_E is very nearly unity, we can write

$$\Delta r_c-\Delta r_0=\left(1-\frac{\sigma_R}{\sigma_E}\right)r.$$

In order for the relative surface tensions to be exactly 1, i.e., to give a horizontal line for the surface tension-concentration curve, it is found that Δr for the 10^{-5} M KCl solution must be 13.6 angstroms greater than Δr for the 10^{-4} M KCl solution, and the latter must in turn be 122 angstroms greater than Δr for the 10^{-3} M KCl solution. If ζ is $+67$ for the 10^{-3} solution, then it would have to be $+66$ for the 10^{-4} M solution, and $+91$ for the 10^{-5} M solution. It does not seem probable that an experimental error of this magnitude could have been made in measuring the zeta-potential of the 10^{-5} M solution.

Since the failure of the Langmuir theory in this instance cannot be attributed to experimental error in the zeta-potential measurements, consideration should be given to the possibility that the charge at the air-solution interface of the wetting film may be large enough to play a more important part in determining the thickness of the wetting film than does the zeta-potential at the silica interface. If instead of the electric potential having its minimum value at the air interface, it has a comparatively high value, there might be a thick film due to this potential even though the zeta-potential has a very low value. As was pointed out by Jones and Frizzell,[3] the Langmuir theory entirely neglects the effect of electric charges and the resulting potential at the air interface on the wetting film thickness. It may be that if the theory is extended to take this potential into account and when information about its magnitude is obtained, then the minimum in the surface tension curve will be satisfactorily explained as owing to the Langmuir-type wetting film with these solutions, just as it was with the same solutions without added thorium.

TABLE VI. Corrected surface tensions.*

KCl conc.	Apparent relative surface tension	Δr (angstrom)	Langmuir correction factor	Corrected relative surface tension
10^{-5}	1.00000	0	—	(1.00000)
10^{-4}	0.99999	277	0.99980	0.99979
10^{-3}	0.99990	194	0.99986	0.99976

* Referred to the solution of $10^{-5}M$ KCl $-10^{-6}M$ $ThCl_4$. This reference solution has the same apparent relative surface tension to that of water as a $10^{-6}M$ $ThCl_4$ solution, namely 0.99995.

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Determination of Free Radicals in Acetone Photolysis

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Acetone has been photolyzed in a flow system at several temperatures in the pressure range 0.5 to 11 mm with exciting radiation of wave-length 2650–2900A and 2537A. The free methyl radicals formed in the decomposition have been determined as lead tetramethyl. Approximately one methyl radical is formed for every four molecules of carbon monoxide, the actual proportion depending on temperature and pressure. Relatively more free radicals are formed at 100°C than at lower temperatures and more are formed at lower pressure than at high. A process involving the existence of a long lived metastable state for photoactivated acetone has been suggested to explain the results. The proposed scheme is found consistent with most of the published work on acetone photolysis.

INTRODUCTION

SUBSEQUENT to the absorption of ultraviolet light, acetone molecules decompose either by rearrangement into the two principal products, ethane and carbon monoxide,[1,2] or by fission into methyl and acetyl radicals which in turn give ethane, biacetyl, and carbon monoxide.[3–5] According to some authors it is unnecessary to consider the rearrangement into ultimate molecules under any circumstances since the main features of the reaction are accounted for in terms of free radicals. The absence of any definite information on the relative importance of the two possible paths of decomposition has given rise to numerous and sometimes contradictory suggestions for the detailed mechanism of the total reaction. To explain different sets of data, for example, various authors have had to suggest several possibilities for the disappearance of the acetyl radicals: formation of biacetyl homogeneously, through bi-molecular and tri-molecular reactions, and heterogeneously on the walls; decomposition of the acetyl radicals both heterogeneously and homogeneously, and both uni- and bi-molecularly; and several combinations of these possibilities.[1,3,6–9] It has also been suggested that the acetyl radicals disappear by reaction with methyl radicals to produce ethane.[5]

A clear-cut decision concerning the behavior of the radicals seems to be impossible until at least the relative importance of the ultimate molecule reaction has been settled. Since the free alkyl radicals can be quantitatively converted into volatile lead compounds by allowing them to pass over lead mirrors,[10] it should be possible in the absence of chain reactions, as is the case in acetone photolysis,[11] to determine exactly what fraction of the products of reaction arises from free radicals and what fraction, if any, comes from rearrangement of the photoactivated molecules. We have undertaken such an investigation.

EXPERIMENTAL

Procedure

Carefully degassed acetone was introduced as a vapor from a storage bulb of the substance and was allowed to flow through a section of quartz tubing surrounded by a Hanovia S 2537 lamp, the radiated energy from which is at least 90 percent

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in the 2537A line. The illuminated acetone was allowed to pass over a mirror of lead deposited immediately adjacent to the lighted section of tubing (except in a few cases where the mirror was further down stream). The mirror was of such length as to give full lead transport[12] at a pressure of 4.4 mm. The gas stream, after it had passed over the mirror, was sent through a trap kept at liquid nitrogen temperatures. The gaseous products not condensed in this trap were removed by a Toepler pump and were analyzed for carbon monoxide, and occasionally also for ethane, in a semi-micro gas analysis apparatus.[13]

Lead Analysis

The determination of the lead alkyl in the cold trap, by dithizone titration, was carried out as previously described.[12] In later experiments (serial numbers above 200), a modified end-point procedure was used which was more convenient and probably more dependable. In this method, an excess of dithizone is added to the sample whose lead content is to be measured and the excess determined by titration with a standard lead nitrate solution. This procedure eliminated the blank corrections necessitated by loss of dithizone in the direct titration.

RESULTS

The experiments were conducted with inlet pressures of 0.5, 2.1, 4.4, and 11.5 mm of acetone and with the illuminated region at 0°, 45°, 60°, 80°, and 100°C. In Table I are recorded the results from the experiments in which the exciting radiation was 2537A.

The volume of gas recorded in Table I is in mm^3 corrected to S.T.P. The amounts of lead are in micrograms. It is assumed, in computing methyl production, that each lead atom transported from the mirror is combined with four methyl groups. One microgram of lead is therefore equivalent to 0.432 mm^3 of CH_3 or 0.216 mm^3 of potential ethane, at S.T.P.

Some of the radicals, however, are not recovered because they disappear on the walls of the tube before they reach the mirror; but the number that escapes detection in this way can be computed through the following considerations. The methyl radicals disappear in a first-order process.[10,12,14] We assume that this process is the same in both illuminated and dark regions. During illumination of acetone, however, radicals are released at a practically constant rate because the fraction of molecules that decomposes is small, actually something in the neighborhood of 10^{-4}. The rate at which methyl radicals accumulate as acetone passes through the illuminated section is

$$d(CH_3)/dt = k_0 - k_1(CH_3), \qquad (1)$$

TABLE I. Photolysis of acetone with 2537A radiation.

No.	T °C	P mm Hg	CO per minute, in mm^3	Pb per minute, in μg	CH_3 per minute, in mm^3	C_2H_6 per minute, in mm^3	$CO/(\frac{1}{2}CH_3+C_2H_6)$	$CH_3 \times 1.12/CO$
45	0	2.1	5.05	4.1	1.78			.39
64			1.42	1.4	.61			.48
239			4.22	2.8	1.21	3.26	1.09	.32
246			4.64	3.4	1.47			.36
								av. .39
244	0	4.4	8.81	5.2	2.25	3.72	1.82	.29
247			8.81	5.6	2.42	3.53	1.86	.31
								av. .30
253	0	11.5	17.2	7.5	3.24	13.6	1.13	.21
254			14.2	6.7	2.90	11.0	1.14	.23
								av. .22
84	45	0.5	1.38	1.9	.82			.67
238			5.09	6.6	2.86	15.1	.31	.63
								av. .65
28	45	2.1	4.04	5.8[b]	2.50			.69
30			4.22	6.3[b]	2.73			.72
58			5.09	4.7	2.04			.45
73			2.11	2.3	1.00			.53
74			1.88	2.1	.91			.54
75			1.97	2.4	1.04			.59
227			5.27	6.2	2.68	6.89	.64	.57
								av. .58
50	45	4.4	6.61	4.8	2.08			.35
								av. .35
51	45	11.5	7.53	5.4	2.34			.35
59			7.53	5.0	2.17			.32
								av. .34
251	65	2.1	12.4	14	6.06			.55
252			13.4	18.4	7.97	12.8	.80	.67
								av. .61
66	80	2.1	4.13	5.3	2.30			.62
230			11.2	13.4	5.80	8.86	.95	.58
								av. .60
38	100	2.1	4.22	5.6	2.42			.64
83			7.99	9.0[a]	3.90			.55
91			8.90	No An.		6.61		
92			8.90	No An.		8.54		
93			12.2	10.6	4.59	10.8	.93	.42
228			3.35	4.4	1.91			.64
234			12.9	19.1	8.27	9.09	.98	.72
235			11.0	14.7	6.37	9.46	.87	.65
248			11.1	14.7	6.37	9.55	.87	.64
95			19.3	No M.		11.5		av. .61
81	100	4.4	6.15	7.8	3.38			.62
82			5.97	7.6	3.29			.62
								av. .62
249	100	11.5	14.6	15.5	6.71	12.2	.94	.51
250			14.7	15.8	6.84	13.8	.85	.52
								av. .52

[a] From two successive mirrors.
[b] From three successive mirrors.
"No An.": lead not determined.
"No M.": no lead mirror.

[12] M. H. Feldman, J. E. Ricci, and M. Burton, J. Chem. Phys. **10**, 618 (1942).
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[14] L. May, H. A. Taylor, and M. Burton, J. Am. Chem. Soc. **63**, 249 (1941).

where (CH_3) is the concentration of methyl radicals at any point, t is the time for the gas to travel from the inlet to that point and k_0 and k_1 are the coefficients of the zero-order formation of radicals for a fixed set of conditions and of the first-order disappearance, respectively. Assuming the pressure gradients to be constant and the expansion that of a perfect gas, t is given by the formula,[15]

$$t=x/v-ax^2/2Pv. \qquad (2)$$

In this equation, x is the distance the gas has travelled, v is the streaming velocity (approximately 3×10^3 cm sec.$^{-1}$ in our experiments), P is the entrance pressure, and a is the pressure gradient along the tube. The value of k_1 was calculated from half-life experiments performed in the same apparatus,[12] being 63 sec.$^{-1}$ when the radicals are formed at 45° and 87 sec.$^{-1}$ for photolysis at 100°C. The coefficient k_0 was then evaluated from the integrated form of Eq. (1), or

$$(CH_3)=[k_0/k_1][1-\exp(-k_1t)], \qquad (3)$$

by substituting the amount of methyl recovered when the mirror was immediately adjacent to the illuminated section of quartz tubing. The total amount of methyl which would be recovered at this point if no disappearance had occurred in the lighted region is then simply k_0t. The calculation based on the experimental figures shows that approximately 12 percent of the radicals disappeared before they were carried away from the lamp. The fraction of radicals thus disappearing in an illuminated zone for which t is not too large is moreover nearly independent of both the temperature and the pressure. The final column in Table I gives "corrected" ratios of CH_3/CO; these are simply the experimental figures increased by 12 percent to allow for the radicals lost before they reached the mirrors.

The column in Table I headed $CO/(\frac{1}{2}CH_3+C_2H_6)$ constitutes a kind of materials-balance for our experiments. If the sole products are carbon monoxide, ethane, and lead tetramethyl, the ratio should be unity. That the average of all the ratios is close to one, with relatively few ratios deviating by more than 20 percent from this figure, is evidence that the principal products are indeed the three substances named. The deviations probably reflect the difficulties of working with micro-quantities of products rather than the formation of important amounts of other substances such as biacetyl.

TABLE II. Photolysis of acetone at 100°C and 2.1 mm, using 2650–2900A.

No.	CO per minute, in mm³	Pb per minute, in μg	CH_3 per minute, in mm³	C_2H_6 per minute, in mm³	$CO/(\frac{1}{2}CH_3+C_2H_6)$	$(CH_3/CO)\times1.12$
209	1.14	[a]		1.26	.90	
211	1.24	[b]		.91		
212	1.31	1.1	.48	.99	1.07	.41
213	1.06	1.0	.43	.87	.98	.45
214	.67	.2	.09	.53	1.17	.15
215	.36	.36	.16	.25	1.09	.50
216	.59	.45	.19	.40	1.19	.36
217	.42	.21	.09	.27	1.33	.24
221	.63	.75	.32	.49	.97	.57
222	.17	[a]		.13	1.3	
223	.59	.43	.19	.40	1.19	.36
224	1.08	1.0	.43	.74	1.13	.45
225	.46	.39	.17	.30	1.19	.41
226	1.86	[b]		2.28		

[a] No lead mirror.
[b] Mirror used, but lead not determined.

Table II contains the experimental results of runs where the activating radiation lies in the region 2650–2900A. A General Electric H-6 lamp was the source of light and the light was filtered by a chlorine-mercuric chloride cell.[16] The runs were made at 100°C with an entering acetone pressure of 2.1 mm.

Completeness of Radical Recovery

Before interpreting these data, it is necessary to consider whether the lead mirrors actually convert all the methyl radicals in the photolyzed vapor into lead tetramethyl. Paneth, Hofeditz, and Wunsch[10b] have shown that over 80 percent of the methyls formed by decomposition of lead tetramethyl are converted by contact with a lead mirror into lead-alkyl. It seems probable that every free radical striking the metal reacts with it. In their experiments, however, Paneth, Hofeditz, and Wunsch tested the behavior of the radicals when all of the reactant was decomposed and only inert carrier gas and radicals came into contact with the mirrors. In our experiments, the radicals accompany a very large excess of undecomposed ketone, and a question arises concerning the completeness of radical recovery under these circumstances.

All the methyl radicals actually present are

[15] F. Paneth and W. Lautsch, Ber. **64**, 2708 (1931).

[16] E. J. Bowen, J. Chem. Soc. 76 (1935).

removed from the gas by a 2 cm mirror[12] and they must be converted either into lead tetramethyl or into ethane, for no other methyl derivatives are formed insofar as we can judge from the materials-balance. It is not easy to picture a specific catalytic effect of acetone in causing the methyl radicals adsorbed on the surface of lead to combine giving ethane rather than lead tetramethyl. Were such an effect in operation, however, it would be pressure dependent; yet at 100° a fivefold increase in pressure leaves the CH_3/CO ratio nearly unchanged. One further possibility must be considered, namely, a conversion of methyls adsorbed on the lead surface into some product other than lead alkyl by reaction with acetone molecules. The observation, however, that a lead mirror has no effect on carbon monoxide production or on the ratio, $CO/(\frac{1}{2}CH_3+C_2H_6)$, means that the methyls cannot disappear by reaction with acetone. We must conclude that all the free radicals reaching the mirror are changed to lead alkyl.

In connection with the calculation of methyl production, we have assumed a maximum alkylation of lead. The formation of less highly alkylated compounds of lead would mean that we have over-calculated the methyl concentrations and that our estimates of the fractions of molecules decomposing by way of free radicals are maxima.

DISCUSSION

The results summarized in Table I, contrary to all previous opinion, indicate that an important part of the acetone decomposition at 2537A occurs as a rearrangement. If the reaction proceeded wholly through free radical formation, the CH_3/CO ratios, under conditions such that all the acetyl radicals decompose, i.e., at high temperature, would have a value of 2. The ratios in all cases are much below this figure, ranging from 0.2 to 0.6. At high temperatures, where it may be assumed that two mirror-active particles are produced per molecule splitting into free radicals, the fraction, α, of decomposing acetone molecules producing free radicals, would be numerically one-half of the mean "corrected" CH_3/CO ratios of Table I. At lower temperatures this fraction, α, would be somewhat greater than half of the tabulated ratio, but it cannot be greater than the ratio CH_3/CO even if the acetyl radicals formed are assumed not to decompose at all. It is evident, therefore, that much of the carbon monoxide is formed unaccompanied by free radical formation, and that the fraction of the total decomposition proceeding through free radical split is low, and of the order of 0.3.

These data make it necessary to explain, in terms of a reaction that proceeds partially by way of a rearrangement, the numerous reported experimental results connecting both quantum yields and products with such variables as pressure, temperature, and intensity. It is not enough to propose two alternative modes of decomposition of activated acetone, one to give radicals, one to give molecules. Such a simple proposal (without introducing the assumption of very effective recombination of the primary radicals, a question which will be discussed below) cannot explain, for example, quantum yields below $(1-\alpha)$, the fraction of molecules undergoing the rearrangement reaction. A somewhat more complex scheme is required. Such a scheme has been suggested by Spence and Wild[1] for the photo-decomposition at 3130A. The Spence and Wild mechanism is consistent with most of the established facts at 3130A. A modification and amplification is here suggested for the reaction at 2537A.

The Spence and Wild Reaction Scheme

The reactions may be summarized as follows:

$$CH_3COCH_3+h\nu\rightarrow CH_3COCH_3^*, \quad (1)$$

$$CH_3COCH_3^*\rightarrow CH_3CO+CH_3, \quad (2)$$

$$CH_3COCH_3^*+M\rightarrow CH_3COCH_3^{**}+M, \quad (3)$$

$$CH_3COCH_3^{**}\rightarrow C_2H_6+CO, \quad (4)$$

$$CH_3COCH_3^{**}\xrightarrow{\text{wall}} C_2H_6+CO, \quad (5)$$

$$CH_3COCH_3^{**}\rightarrow CH_3COCH_3. \quad (6)$$

Briefly this scheme suggests that photo-activated acetone molecules either decompose in a relatively short time to give radicals or are converted (by collision) into a metastable state from which they may escape by collisional deactivation or by rearrangement into molecules.[17] The lifetime

[17] In photolytic reactions, the principle of least motion as proposed by Rice and Teller (J. Chem. Phys. 6, 489 (1938)),

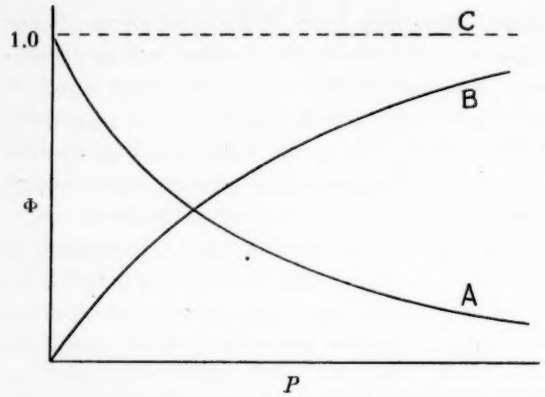

FIG. 1. Relationships in acetone photolysis at 100° (schematic). *A*: free radical split; *B*: ultimate molecular rearrangement; *C*: total decomposition.

of the metastable molecules produced by radiation of wave-length 3130A, is, according to the estimates of Spence and Wild, in the neighborhood of 10^{-2} sec. The life of the initially activated molecules, however, must be very short as shown by the complete diffuseness of the absorption spectrum.[18]

The efficiency of various types of molecules in bringing about the transition of excited molecules to the long lived state cannot be predicted. Nor can their efficiency in inducing rearrangement or deactivation be accurately estimated prior to actual experiments. It is only possible to suppose that the effectiveness will depend on the type of molecule and on the temperature.

If one rejects consideration of collisional deactivation, the low quantum yields under ordinary conditions must be ascribed to recombination of the initially formed radicals.[19] The reaction-complex of methyl and acetyl according to this view must undergo a transition to acetone with much greater efficiency than a similar association of two methyl radicals to give ethane or two acetyl radicals to give biacetyl. Under some conditions, the quantum yields are as low as 0.2, which would mean recombination of 80 percent of the primary radicals. The specificity of the reaction, (i.e., the efficiency compared with the total of all other possible reactions of these radicals) would mark this photolysis as unusual. It would be a striking circumstance not merely that the photo-activated molecules should be so unstable that all of them decompose in $\sim 10^{-8}$ sec., but that the radicals would endure long enough to enter this process almost exclusively. Although the higher energy content of the initially excited molecules as compared with the united radicals, which have only thermal energy, would lead to greater instability of the former, the yield needed to explain the result would have to be so great that some alternative way of accounting for them seems desirable. In our own experiments, the carbon monoxide yield is not affected by the mirrors beyond a matter of 5 to 10 percent, and that result is possibly attributable to other variations. The removal of methyl radicals from the gas mixture with consequent elimination of union of methyl and acetyl radicals does not change the basic course of the reaction. In other words the recombination of methyl and acetyl radicals is unimportant in our experiments, although it may occur under other conditions.[20]

EFFECTS OF EXPERIMENTAL VARIABLES ON THE REACTION

At a given wave-length, the proportion of excited acetone which undergoes a free radical split and the proportion that rearranges, will be a function of the acetone pressure and of the temperature. The probable relations are shown

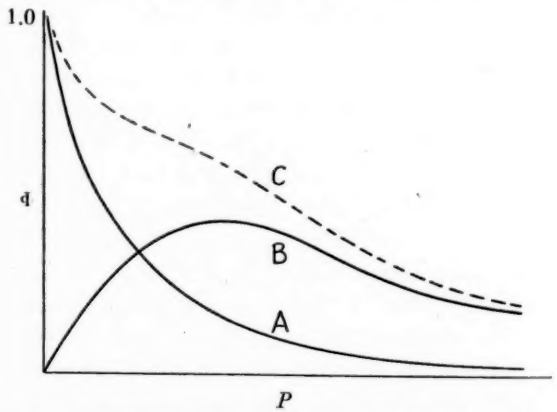

FIG. 2. Relationships in acetone photolysis at room temperature (schematic). *A*: free radical split; *B*: ultimate molecular rearrangement; *C*: total decomposition.

according to which the lighter ketones would not be expected to rearrange directly into stable products, is not strictly applicable as, indeed, Rice and Teller themselves point out (page 496). Consequently we are basing our discussion on the experimental findings.

[18] R. G. W. Norrish, H. G. Crone, and O. D. Saltmarsh, J. Chem. Soc. 1456 (1934).

[19] H. S. Taylor and J. C. Jungers, Trans. Faraday Soc. **33**, 1353 (1937), suggest that part of the effect is due to the reaction $(CH_3CO)_2+CH_3 \rightarrow CH_3COCH_3+CH_3CO$.

[20] Cf. K. Faltings, Ber. **72**, 1207 (1937), who found acetone to be formed with a quantum efficiency of ~0.1 when ethane is photolyzed in the presence of carbon monoxide.

schematically in Fig. 1 for high temperatures (100°C) and in Fig. 2 for room temperature. At very low pressures the decomposition will be completely effective in producing free radicals, for in the absence of collisions, the unstable molecules can do nothing else but split in this way. As the pressure increases, more and more of the activated molecules will be sent, as a result of collision with other gaseous molecules, into a long lived state. At high temperature, it is assumed that practically all the molecules in this photo-activated metastable state decompose because of their great internal energy, so that the total quantum yield (or the efficiency of the total decomposition) should remain substantially at unity at all pressures. At lower temperatures however, the rearrangement passes ultimately through a maximum because of the increasing importance of collisional deactivation. At those temperatures, therefore, where quantum yields are appreciably less than unity, the quantum yields would probably continue to fall with increasing pressure, and would approach zero as a limiting value.

While the experimental quantum yields do not reach unity at ordinary temperature, it is true that several investigators have found that quantum yields increase rapidly below 50 mm pressure both at 2537A and at 3130A. Yields at the longer wave-length are smaller than at shorter under comparable conditions because the less energetic molecules are more apt to be deactivated by collision before decomposition. Despite the drop in quantum yield, experimental values of the ratio CH_3/CO are about the same at the two different wave-lengths (Tables I and II); apparently, a molecule which has absorbed a quantum at $\lambda = 3130$A must have both a smaller chance of a split into radicals in a given time and a correspondingly greater chance of entry into a metastable state.

The effects of pressure and temperature on the experimental ratio, CH_3/CO, may be discussed on the basis of these curves. That this ratio should fall with increasing pressure follows at once from the effect of pressure on the two competing paths of decomposition as shown on Figs. 1 and 2. In Fig. 3 the average of the observed ratios, CH_3/CO, (Table I) is plotted as function of pressure for the three principal temperatures

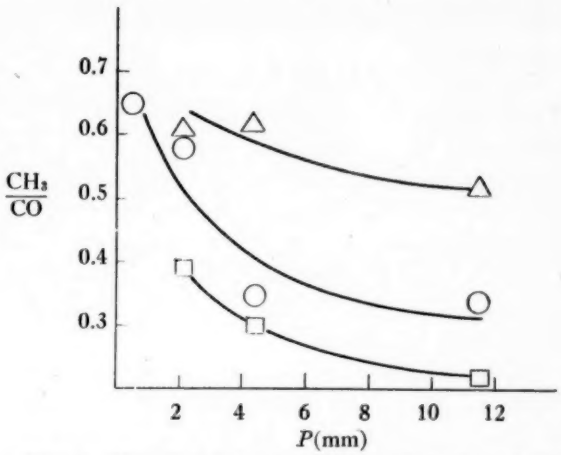

FIG. 3. Observed ratio, CH_3/CO, as function of pressure, at 2537A. Squares: 0°C; circles: 45°C; triangles: 100°C.

studied. As expected according to the proposed scheme, the ratio rises with decreasing pressure, at each temperature, and may be expected to reach the theoretical value of 2 as a limit. The actual shape of the curves drawn, however, does not have great significance, since the uncertainty of each point is rather large. It would be difficult to predict how the effect of pressure should change with the temperature, since a rise in temperature would presumably increase the efficiency of both paths relative to deactivation. The figure shows that the ratio increases with rising temperature, especially at the higher pressures, in spite of the greater efficiency of the rearrangement reaction at higher temperature. This state of affairs may result partly from a greater proportion of the initial reaction giving free radicals (even though the collision frequency at a given pressure is increased) but more especially from an increase in the average number of methyls arising from a molecule undergoing the free radical split. There seems to be considerable evidence that acetyl radicals become almost completely unstable at 100°C, so that two methyls would be formed from each acetone decomposing in this way, whereas an average of less than two per molecule would be formed at lower temperatures. The fraction, α, of the total decomposition proceeding through the free radical path would therefore be half of the observed CH_3/CO ratio at 100°C, and somewhat greater than half this ratio at lower temperatures, depending on the probability of reactions of

CH_3CO other than decomposition yielding CH_3 as a product.

The effect of narrower tubes (a decrease in size of tube results in increase of the ratio C_2H_6/CO)[3a] appears to be to leave the free radical process substantially unchanged but to increase the total quantum yield by inducing rearrangement of the metastable molecules. At 100°C, where the total quantum yield is about unity anyway, the effect of changes in the geometry of the apparatus should be a minimum.

There is some question of how the quantum yields are affected by a diminished light intensity. If there is any effect at all, it is to increase the yield at low intensities. While Spence and Wild did not discuss this effect, it can be explained on the basis of some reaction of activated molecules with products, such as radicals, other activated molecules and final products of the reaction. It seems very likely that biacetyl in particular would account for the decrease in yield with rising intensity. The transfer of the excitation energy from acetone to biacetyl would be accompanied by a corresponding increase in light emission from the latter. Since fluorescence is observed[21] even above 100°C, there should be some intensity effect on quantum yields at 100° although this would be difficult to observe.

There have been numerous reports of the effects of foreign gases on the reaction. The effect of iodine,[5,9] carbon dioxide,[3b] oxygen,[22] hydrogen,[4,23] propane,[7] deutero-biacetyl,[24] and nitric oxide[8] have been investigated. Some of these experiments have been cited in support of a complete radical mechanism; but it is in these cases especially that the course of the reaction is very seriously changed, as, for example, when nitric oxide is introduced. In each case, however, it seems necessary to consider specific reactions between acetone molecules in the metastable state and the admixed gas. Thus the extremely efficient production of iodides suggests two important reactions, namely,

$$CH_3COCH_3^{**}+I_2\rightarrow 2CH_3I+CO, \quad (7)$$

$$CH_3COCH_3^{**}+I_2\rightarrow CH_3I+CH_3COI, \quad (8)$$

which might be considered together with the reaction

$$CH_3CO+I_2\rightleftarrows CH_3COI+I, \quad (9)$$

suggested by Gorin to explain the dependence of iodide production on the concentration of iodine.[5]

Other Radical Reactions

Since all of our measurements of free radical concentrations are based on the idea that the disappearance reactions are the same in the illuminated region as beyond, it seems desirable to consider certain reactions which might lead to an extra fast clean-up in the illuminated region. One of the possibilities arises from Gorin's conclusion[5] that acetyl radicals are stable at 100°, disappearing at that temperature not so much by decomposition as by reaction with methyl radicals,

$$CH_3CO+CH_3\rightarrow C_2H_6+CO. \quad (10)$$

This reaction would be not only an additional source of ethane but also an outlet for methyl radicals. It may be argued that some, perhaps a large fraction, of these radicals disappear in this way at 100° and so are not picked up by the mirrors. Were this bimolecular reaction contributing significantly to the over-all changes, however, it would be much more important at high radical concentrations than at low. A five-fold change in concentration of the radicals, as measured by the rate of carbon monoxide production, causes nothing greater than a 30 percent change in CH_3/CO ratio at any temperature and only a 20 percent change at 100°. We must conclude that reaction (10) is not important in our experiments. For similar reasons, the reaction,

$$CH_3CO+CH_3CO\rightarrow C_2H_6+2CO, \quad (11)$$

cannot have an important role in our experiments.

The union of methyl and acetyl radicals to reform acetone, moreover, can have no effect on the interpretation of results in Tables I and II because such a union can affect only the quantum efficiency of the total process and not the distribution of products. The formation of biacetyl

$$CH_3CO+CH_3CO\rightarrow(CH_3CO)_2 \quad (12)$$

cannot account for small values of CH_3/CO but on the contrary should lead to ratios greater than

[21] W. A. Noyes and F. C. Henriques, J. Chem. Phys. **7**, 767 (1939).
[22] P. Fugassi, J. Am. Chem. Soc. **59**, 2092 (1937); F. O. Rice and C. E. Schildknecht, J. Am. Chem. Soc. **60**, 3044 (1938).
[23] W. West, J. Am. Chem. Soc. **57**, 1931 (1935).
[24] D. S. Herr, M. S. Matheson, and W. D. Walters, J. Am. Chem. Soc. **63**, 1464 (1941).

unity. While biacetyl seems not to make up more than a minor part of the products, each biacetyl molecule removes two potential molecules of carbon monoxide from the products and its effect would be to increase the net CH_3/CO ratio.

Another type of reaction which might be of importance within the illuminated zone but not outside involves hot radicals, that is, energy-rich radicals emerging from decomposing acetone molecules. The behavior of such radicals from propionaldehyde has been considered by Garrison and Burton.[25] The chief effect of such hot radicals, may be to induce rearrangement of other acetone molecules to give stable products. If the initial reaction of excited acetone molecules, however, produced in every case two such hot radicals, quantum yields should be three rather than <1 as observed. Furthermore, even if all the initial splitting gave rise to such specially active radicals, there would still be more CO produced than corresponds to recovered radicals.

We have omitted from the reaction list those reactions which follow the initial free-radical split. There are numerous possibilities for formation of ethane, biacetyl and carbon monoxide. These possibilities have already been extensively discussed in the literature and the present work affords little additional information concerning them.

CONCLUSION

Most of the photochemical studies of acetone can be explained satisfactorily (in the absence of free radical determinations) either by a completely free radical mechanism or by a mechanism such as that of Spence and Wild. The particular interest in the present work is that the free radicals have been counted and the actual proportion of reaction proceeding through radical intermediates has been estimated quantitatively. Decision as to the secondary free radical reactions must as before depend on kinetic studies. Likewise, opinions concerning the behavior of the metastable state must be based on experimental determination of quantum yields, fluorescence and nature of the products. Nevertheless, the Spence and Wild scheme apparently is consistent with published data, for 2537A.

[25] W. M. Garrison and M. Burton, J. Chem. Phys. **10**, 730 (1942).

COMPARISON OF PROPIONALDEHYDE AND ACETONE PHOTOLYSIS

The experiments of May, Taylor, and Burton[14] indicated that equal numbers of free radicals are released when propionaldehyde or acetone vapors are photolyzed under comparable conditions. It was argued that this identity, assuming the same quantum yields, means that if one photolysis is an exclusively free radical process the other must also be such. It was later found, however, that the only mirror-active particles formed in the photolysis of propionaldehyde are ethyl radicals,[25] and there can be only one such radical coming from one molecule of the aldehyde. But an acetone molecule may give either one or two methyl radicals and on the average will give something between. The experiments of May, Taylor, and Burton were conducted at a temperature (about 55°C)[26] where the acetyl radicals produced from acetone may be considered to be at least partially if not completely decomposed. The observed approximate equality in mirror activity then cannot be consistent with a 100 percent free radical mechanism for acetone, if the quantum yield of the two photolytic decompositions is approximately the same. On the basis of such an assumption, the observation involved would be further interesting evidence of the reality of the results here reported, which indicate so strongly that the photolysis of acetone does not proceed exclusively through free radical formation. The observation of May, Taylor, and Burton would mean either that both processes involve partial free radical formation or that at least the acetone photolysis does. A determination of the quantum yields, then, of the two decompositions under the conditions of the experiments of May, Taylor, and Burton, would be of interest; if the quantum yield of the propionaldehyde photolysis is not greater than twice that of the acetone it follows that some of the acetone must decompose without production of free radicals. The data of Garrison and Burton for the ratio C_2H_5/CO in propionaldehyde photolysis[25] show that about 45 percent of the propionaldehyde molecules producing carbon monoxide also produce ethyl radicals (allowance being made for about 25 percent disappearance of radicals in the illuminated zone).

[26] L. May, Thesis, New York University, March, 1941.

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Some Observations on the Theory of Contact Angles

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August 27, 1945

IF a plane solid surface is dipped into a large liquid surface, a meniscus is formed. The shape of this meniscus is governed by the law:

$$1/R_1+1/R_2=\rho g y/\sigma_l, \tag{1}$$

where the R's are the principal radii of curvature of the liquid surface, ρ is the density, g the acceleration of gravity, y is the height of the meniscus at any point, and σ_l is the free surface energy of the liquid surface.

If the work necessary to stretch the liquid surface and to raise the water is calculated, the following expression is obtained:

$$\frac{\sigma_l}{3a}[2\sqrt{2}-(2-a^2h^2)^{3/2}]+\sigma_l h\cot\Gamma\left(1-\frac{a^2h^2}{3}\right), \tag{2}$$

where h is the height of the meniscus at the point of contact with the solid, Γ is the angle of tilt of the solid surface with the horizontal, and:

$$a^2=\rho g/2\sigma_l.$$

The free energy available to do the work is given by the expression:

$$(\sigma_{sa}-\sigma_{sl})\frac{h}{\sin\Gamma}, \tag{3}$$

where σ_{sa} is the free surface energy the solid-air interface, and σ_{sl} is the free surface energy of the solid-liquid interface. These two expressions are not equal. However, if Eq. (3) is differentiated with respect to Γ and the resulting equation set equal to zero, the derivative of h with respect to Γ is obtained. If Eq. (2) plus an unknown factor, $f(h, \Gamma)$, is also differentiated with respect to Γ and set equal to zero and the expression for $dh/d\Gamma$ substituted in this second differentiation, the necessary terms to be inserted in (2) to make it equal to (3) are obtained. Since this is an extreme condition it is the necessary and sufficient condition for equilibrium. The additional terms inserted in expression (2) are exactly the terms obtained by calculating the reversible work done on the slide to rotate it from the angle Γ_0, where $h=0$, to the angle Γ. If we write

$$\cos\alpha_0=\frac{\sigma_{sa}-\sigma_{sl}}{\sigma_l}=\text{a constant}, \tag{4}$$

the final equation takes the form

$$\frac{h}{\sin\Gamma}\cos\alpha_0=\frac{1}{3a}[2\sqrt{2}-(2-a^2h^2)^{3/2}]+h\cot\Gamma\left(1-\frac{a^2h^2}{3}\right)+\int_{\Gamma_0}^{\Gamma}\left(\frac{2a^2h^2}{3\sin^2\Gamma}+h\frac{\sin\alpha}{\sin\Gamma}\right)d\Gamma, \tag{5}$$

where α is the angle of contact and is a function of h and Γ.

Experimentally Eq. (5) is obeyed well within the limits of error for measurements on paraffin against water. This is all that is necessary to show, for *plane* solid surfaces intersecting a liquid in such a manner that one of the principal radii of curvature of the meniscus is infinite, that differences in the advancing and receding contact angles are impossible providing α_0 is constant.

If the two principal radii of curvature of the liquid surface are both finite, an additional variable but not an additional equation of condition is introduced; the system then becomes univariant instead of non-variant and a difference between the advancing and receding contact angles becomes possible.

A more complete paper on this subject will appear later.

The Constitutional Difference Between α- and β-Derivatives of Naphthalene

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August 21, 1945

THE difference with respect, e.g. to the bond distance, electric dipole moment, etc., for chlorine, bond to a saturated carbon atom, or to a carbon atom carrying multiple bonds as in the substituted ethylene and benzene derivatives was explained as due to a partial double bond character in the latter case.[1] In order to see whether the rather crude method of approach[2] used before would be also valuable in explaining finer constitutional details, an analogous calculation was set up for α- and β-chloronaphthalene, respectively.

The complete results will be published elsewhere, here only some conclusions will be given. For the energy difference between the ground state and the first excited state, corresponding to the long wave limit of the U.V. absorption we calculated 1.1502β and 1.1629β for the α- and β-derivative, respectively, as compared with 30845 cm^{-1} and 31130 cm^{-1} [3] found experimentally. The correspondence is quite remarkable. The double bond character for the C—Cl bond was calculated as 14.17 percent and 12.98 percent, respectively (12.6 percent for monochlorobenzene).

For the electric dipole moment of both molecules we may calculate (using an effective electronic charge[4] that gives the right experimental value for the α-compound) $\mu_\beta-\mu_\alpha=0.06$. Experimentally: Parts[5] 1.59 resp. 1.72; Nakata[6] 1.50 resp. 1.57 for α- and β-chloronaphthalene. Both the sign and the magnitude are correctly given by the theory.

For negative atoms with p_z electrons other than chlorine, e.g., oxygen and nitrogen atoms, qualitatively the same result will be obtained indicating a larger double bond bond character for the α-derivative. According to current conceptions[7] this would lead to a lesser basic strength for α-naphthylamine as compared with the corresponding β-derivative. This conclusion is corroborated by the experimental evidence.

α-naphthylamine	$K=0{,}836$	$10^{-10,3}$
β-naphthylamine	$K=1{,}29$	10^{-10}.

The higher amount of double bond character as calculated for the α-derivative as compared with β-chloronaphthalene, etc., is thus found to be in complete accordance with various experimental evidence. We feel justified to conclude that the molecular orbital treatment in the crude form used here is able to account even for minor details of molecular constitution.

[1] J. A. A. Ketelaar, Rec. trav. chim. **58**, 266 (1939). J. Sherman and J. A. A. Ketelaar, Physica **6**, 572 (1939).
[2] G. W. Wheland and L. Pauling, J. Am. Chem. Soc. **57**, 2086 (1935).
[3] H. G. de Laszlo, Proc. Roy. Soc. **A111**, 355 (1926).
[4] L. E. Sutton, Trans. Faraday Soc. **30**, 789 (1934). J. A. A. Ketelaar, Rec. trav. chim. **58**, 311 (1939).
[5] A. Parts, Zeits. f. physik. Chemie **B10**, 264 (1930).
[6] N. Nakata, Ber. **64**, 2059 (1931).
[7] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), p. 192.
[8] N. F. Hall and M. R. S. Sprinkle, J. Am. Chem. Soc. **54**, 3469 (1932).

An Absolute Method for the Determination of the Area of a Fine Crystalline Powder

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AND
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July 12, 1945

IN a letter in this Journal[1] with the above title the writers presented a very accurate method for the determination of the area of a very fine solid by a calorimetric method. The results obtained by this method were found to be in excellent agreement with those given by the method of Emmett and the application of the theory of Brunauer, Emmett, and Teller.[2] In this work a crystalline powder is first outgassed and then exposed to the saturated vapor of any liquid which gives a duplex film on the surface of the solid. This film has the same surface energy as the liquid itself and with water is about 25A, or nearly 8 molecules thick. The area of the film-coated powder is found from the total heat in ergs evolved when the powder is dropped into and dispersed in the liquid in a sensitive calorimeter.

In a letter to *The Journal of Chemical Physics* Hans M. Cassel[3] expresses agreement with the theory of this method. He fears, however, that when water is the liquid, the adsorption of the duplex film will give adhesion between the crystals which "may cause inseparable clusters to form." To the writers it appears that Cassel has two objections to the experimental application of the method: (1) the formation of clusters, which do not disperse in the liquid, and (2) the effect of capillary condensation, which reduces the area of the duplex film.

As to (1), Cassel's references to Tomlinson[4] and Stone[5] give evidence against his own idea, in the more complete work of Stone. In considering (2), Cassel states "this point has been overlooked" by Harkins and Jura. Had he read our papers carefully he would have known that this statement is not true, since it is discussed in J. Am. Chem Soc. **66**, 926–7 (1944).

From a careful consideration of this particular problem we are able to state that with powders of the degree of fineness thus far used this method is far more accurate than any other; its only disadvantage is its difficulty. The error due to capillary condensation is so small that it is unimportant.

1. While the adsorption is taking place there is mostly point contact between the crystals, since only about one-tenth of the space in the mass of crystals is occupied by them, while nine-tenths is empty space. This condition makes capillary condensation a very slow process.

2. To adsorb a duplex film the mass of crystals is exposed to saturated vapor for a number of hours. The energy of immersion when the film is adsorbed at 96 percent of saturation, where only half as much water is adsorbed, is only 3 percent higher than at the saturation pressure. A decrease as small as 3 percent with an increase of vapor pressure from $p/p_0=0.96$ to $p/p_0=1$ is possible only if the area remains essentially constant in this region, since a decrease of about this magnitude is to be expected to occur from the considerable thickening of the film itself by adsorption without any effect of capillary condensation.

3. The fact that the effect of capillary condensation is shown by Fig. 1, which gives the heat of emersion of a sample of anatase (covered with various thicknesses of water) as determined by (a) direct calorimetric measurements and by (b) calculation of the heat from the adsorption isotherm. *The agreement is excellent, although the effect of capillary condensation* would be to make the calorimetric value low and the adsorption value high. In the adsorption method the energy due to capillary condensation is included, making the value high if capillary condensation is appreciable, while it lowers the area and thus the calorimetric heat. Thus, the agreement between the two methods shows that capillary condensation is so small as not to affect the area obtained by the calorimetric method.

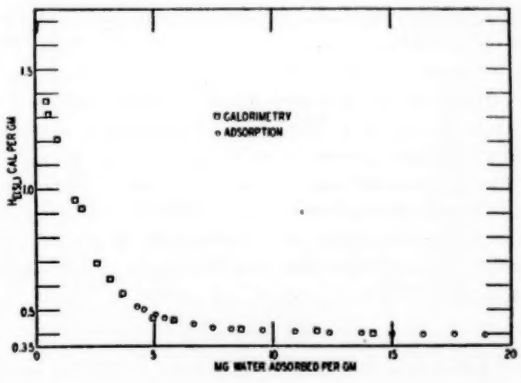

FIG. 1.

4. Concrete experimental evidence that capillary condensation does not play an important role in adsorption on non-porous surfaces is shown by the work of Bangham and Mosallam, who showed that the adsorption of benzene on cleaved mica sheets was the same even at the highest vapor pressures, whether the sheets were separated by fine wires or bound tightly together.

Other evidence which shows that the effect of capillary condensation is so small that it may be entirely neglected will be presented in later papers, since it is too lengthy to be given here.

[1] W. D. Harkins and G. Jura, J. Chem. Phys. **11**, 430 (1943).
[2] S. Braunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).
[3] H. M. Cassel, J. Chem. Phys. **13**, 249 (1945).
[4] G. A. Tomlinson, Phil. Mag. **6**, 695 (1928).
[5] Stone, Phil. Mag. **9**, 610 (1930).

Birefringence of Polyisobutylene in Solution and the Frenkel Theory of Macromolecular Rupture

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THE problem of the shape of dissolved macromolecules has long held the attention of many investigators because of its important bearing on the questions of macromolecular structure, branching, deviations from the Einstein viscosity formula, and the shear stability of the solute under certain conditions of viscous flow. In a recent paper[1] Zvetkov and Frisman have published experimental data showing how the birefringence Δn of various samples of polyisobutylene, dissolved in a hydrocarbon solvent, depends on the velocity gradient g. Their curves (Fig. 11 in their paper) show that for a polyisobutylene sample of sufficiently high molecular weight, the dependence $\Delta n = f(g)$ is already curvilinear at the smallest observable velocity gradients ($g \sim 100$ sec.$^{-1}$) and that there exists a definite value of g at which the slope of the curve increases more or less abruptly. The magnitude of this value of the gradient is higher the lower the viscosity of the solution, and therefore the lower the hydrodynamic force acting on the molecule in flow.

Recognizing that linear macromolecules are ruptured under the influence of sufficiently high shear forces, Zvetkov and Frisman have attempted to account for the shape of their curves on the basis of a theory, recently published by Frenkel,[2] in which it has been proposed that a critical velocity gradient g_k exists at which the coiled chain becomes rod-like in its central portion, and above which rupture will occur. The theoretical value of g_k is related to the viscosity η, the effective radius r of a monomeric chain unit, the length l of a monomeric link, and the degree of polymerization N, according to

$$g_k = 4kT/6\pi\eta r(lN)^2. \qquad (1)$$

For a polyisobutylene sample of average molecular weight 132,000 as determined by the Staudinger formula, Zvetkov and Frisman applied Eq. (1) and found $g_k \leqq 500$ sec.$^{-1}$, in good agreement with the point of steep ascent in their corresponding curve.

As this agreement might be regarded as supporting the theory of rupture, it is felt advisable to call attention to two possible sources of error. (1) Zvetkov and Frisman were apparently unaware that polyisobutylene solutions do not obey the Staudinger formula[3] over a wide range in molecular weight. The true molecular weight of their particular sample, if determined by osmotic pressure measurements, would be of the order of 10 times as large as the value they employed, and substitution of this in Eq. (1) would reduce g_k by roughly 100-fold, in disagreement with their experimental observations. (2) In deriving Eq. (1) Frenkel has assumed that, in the process of rupture, the central chain link in the macromolecule is extended in accordance with Hooke's law. This is not only physically unlikely and quantitatively erroneous but, what is more important, his final relationships leading to Eq. (1) appear to depend for their "catastrophic" form on the analytical linearity of Hooke's law as well as the assumed validity of the latter for bond extensions as large as $\Delta l \sim l$,[4] even though Frenkel admits that under conditions of rupture Hooke's law can no longer be applied. These facts suggest that the agreement between experiment and theory indicated by Zvetkov and Frisman is fortuitous, and that in order to account for the point of a steep ascent in the birefringence curve it is probably necessary either to find a different cause or to develop a theory of rupture which places greater emphasis on the force law governing the extension of the valence linkages. Results obtained in these laboratories[5] with ordinary and fractionated samples indicate that the shear degradation characteristics of polyisobutylene in solution display a more complex behavior, in their dependence on temperature, solvent, and molecular weight, than that suggested by Eq. (1).

[1] W. Zvetkov and E. Frisman, Acta Physicochim. U.S.S.R. **20**, 61 (1945).
[2] J. Frenkel, Acta Physicochim. U.S.S.R. **19**, 51 (1944).
[3] P. J. Flory, J. Am. Chem. Soc. **65**, 372 (1943).
[4] The writer is indebted to Dr. R. F. Tuckett for an interesting discussion of this point.
[5] J. I. Wasson, unpublished data.

Inversion of Low Angle Scattering Data for Particle Size Distribution

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THE purpose of this note is to indicate how the expression for the observed intensity as a function of the scattering angle, which involves an integral over the desired particle size distribution, may be inverted in a straightforward manner.

The equation generaly used for the ratio of scattered. to primary intensity is of the form:

$$I/I_0 = K\int_0^\infty p^2 N(R) \exp(-a^2R^2k^2)dR, \qquad (1)$$

where $a^2 = .221$ (Biscoe and Warren), $k = (4\pi \sin \theta/2)/\lambda$, R

is the radium of gyration of the particle, $N(R)$ is the number distribution in radii, p is the number of electrons per particle, and K contains fundamental and apparatus constants, as well as the polarization factor. Since

$$N(R)(4\pi R^3)/(3d_0)=M(R),$$

the mass distribution, and

$$p^2=((4/3)\pi R^3 d)^2,$$

where d_0 is the mass density and d is the electron density, Eq. (1) reduces to:

$$I/I_0=K^1\int_0^\infty R^3M(R)\exp(-a^2R^2k^2)dR. \quad (2)$$

To obtain $M(R)$, substitute $x=a^2k^2$, and $y=R^2$; the equation can then be inverted according to well-known methods of Laplace transforms. In practice, instead of so deducing distributions, ranges in particle radii are determined by measuring slopes of the curve obtained by plotting log (I/I_0) against k^2. However, Eq. (1) follows from an approximation introduced in order to simplify the process of reducing the data.[1]

For spherical particles, "widely and randomly separated to produce incoherency in the radiation from individual particles," the ratio of secondary to primary intensity is:[2]

$$I/I_0=(e^2/mc^2)^2\frac{1+\cos^2\theta}{2}\int_0^\infty N(R)p^2\phi^2(kR)dR, \quad (3)$$

where

$$\phi(x)=(3/x^2)((\sin x/x)-\cos x).$$

The replacement of ϕ^2 by the exponential which appears in Eq. (1) is unnecessary since it is possible to invert Eq. (3). After correcting the original data for polarization, finite slit length, etc. the expression for the intensity may be rewritten,

$$F(2k)/K''\equiv k^3(I/I_0)_{\text{corrected}}=K''\int_0^\infty N(R)R^3J_{3/2}^2(kR)dR, \quad (4)$$

where

$$K''=(e^2/mc^2)^2 8\pi^3 d^2,$$

since

$$J_{3/2}(x)=(2/\pi x)^{\frac{1}{2}}((\sin x/x)-\cos x).$$

Employing the generalized Neumann integral,[3] the above equation reduces to:

$$F(2k)=(2/\pi)\int_0^\infty N(R)R^3\int_0^{\pi/2}J_3(2kR\cos q)dqdR, \quad (5)$$

Eq. (5) may be rewritten in the form of the Schlömilch integral equation after changing the order of integration:

$$F(2k)=(2/\pi)\int_0^{\pi/2}G(2k\cos q)dq, \quad (6)$$

where

$$G(z)=\int_0^\infty R^2N(R)\cdot RJ_3(zR)dR. \quad (z=2k\cos p). \quad (7)$$

The Hankel transformation[4] permits one to express the number distribution in terms of an integral over $G(z)$,

$$R^2N(R)=\int_0^\infty zG(z)J_3(zR)dz; \quad (8)$$

whereas $G(z)$ may be expressed as an integral involving $F(2k)$:[5]

$$G(2k)=F(0)+2k\int_0^{\pi/2}\frac{\partial}{\partial(2k)}[F(2k\sin q)]dq. \quad (9)$$

Admittedly, the procedure in reducing the data is somewhat involved. The program consists of the following steps:

(a) Convert the photographic density to $(I/I_0)_{\text{corrected}}$.
(b) Plot $F(2k)$; plot the derivative of F with respect to $2k$, *vs.* $2k$.
(c) Replace the argument in the latter by $(2k\sin q)$, and thus get a family of curves, one for each value of $2k$, as functions of q.
(d) Integration according to Eq. (9) gives $G(2k)$.
(e) Replot $G(2k)$ as a function of z; integration according to Eq. (8) gives $N(R)$.

That the original Eq. (3) may be applied only to a dilute suspension of spherical particles should be stressed. It is not valid where the separation between the particles approaches the order of magnitude of the mean radius. Therefore, there is some question as to the significance of particle size distributions based on this method which have been presented in the literature. In the case where the holes are dimensionally comparable to the particles, a straightforward analysis and inversion procedure have been formulated by Professor P. Debye.[6] What is significant then is the fluctuation of the product of electron density at two points separated by R, as these points scan the available volume of diffraction.

I wish to thank Dr. J. M. Richardson for discussions pertaining to the inversions used.

[1] For a simple discussion refer to Louis A. Pipes, J. App. Phys. **10**, 172, 258, 301 (1939).
[2] J. Biscoe and B. E. Warren, J. App. Phys. **13**, 371 (1942).
[3] G. N. Watson, *Treatise on the Theory of Bessel Functions* (The Macmillan, New York, 1944), p. 150.
[4] M. A. Stone, *Linear Transformations* (American Mathematical Society Colloquium Publications, 1932), Vol. XV, p. 110.
[5] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1940), p. 229.
[6] Private communication.